Supporting Information

for

Room-Temperature Near-Infrared Phosphorescence of a Bismuthinidene N,C,N Pincer Complex

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1. Acknowledgements and Contributions

Synthesis and characterization of the compounds and investigation of the absorptive and emissive properties were conducted by K. L. Deuter and in part by D. J. J. Balaba. SC-XRD data acquisition and processing was conducted by K. L. Deuter. Computational investigations using gaussian 16 were conducted by K. L. Deuter and ORCA calculations were conducted by K. L. Deuter under the direction of M. Linseis. The manuscript was prepared by K. L. Deuter with input from all authors. K. L. Deuter and R. F. Winter conceived the project and R. F. Winter supervised the research. The authors acknowledge support by the state of Baden-Württemberg through bwHPC and the German Research Foundation (DFG) through grant no INST 40/575-1 FUGG (JUSTUS 2 cluster), and the NMR Core Facility at the University of Konstanz for experimental support and spectrometer upkeep. K. L. Deuter would like to thank Moritz Nau and Luisa Rieger for proofreading early versions of this manuscript and Johannes Ehlert and Elias Weiße for the synthetic post-production of **LBi** as part of their undergraduate studies.

2. General Methods

Syntheses of all compounds were carried out according to modified literature procedures (see below), using standard Schlenk techniques or a nitrogen-filled glovebox when specified. Solvents (benzene, THF, Et_2O, ^{n}hexane) were dried over a *MBRAUN* solvent purification system (SPS) and kept over molecular sieves (4 Å) and stored under nitrogen atmosphere prior to use. Water contents were determined to be <2 ppm using a Karl-Fischer-Coulometer from *SI Analytics* in regular time intervals. Other solvents (C_6D_6, 2-MeTHF) were dried over molecular sieves (4 Å). Commercially available starting materials were used as received.

^{1}H-NMR spectra were measured on a Bruker Avance III 400 Spectrometer (B_H = 400 MHz), a Jeol 500 Spectrometer (B_H = 500 MHz), and a Bruker Avance III 600 Spectrometer (B_H = 600 MHz) at r.t. in CD_2Cl_2, $CDCl_3$, C_6D_6 or DMSO-d_6. **^{13}C-NMR** spectra were recorded on a Bruker Avance III 600 Spectrometer (B_C = 151 MHz) or on a Bruker Avance III 400 spectrometer (B_C = 101 MHz) in CD_2Cl_2 and C_6D_6. All spectra were referenced against the residual protonated solvent (^{1}H, δ = 5.32 ppm for $CHDCl_2$, 7.16 ppm for C_6D_5H, 7.26 ppm for $CHCl_3$, and 4.79 ppm for DMSO. NMR spectra of **LBi** were recorded in custom-built 5 mm boroeco 5-7 NMR tubes fitted with a J .YOUNG`s Teflon cap and an insert.

Elemental analysis. A C, H, N-analyzer (model Elementar vario MICRO Cube) by Heraeus was used for combustion analyses.

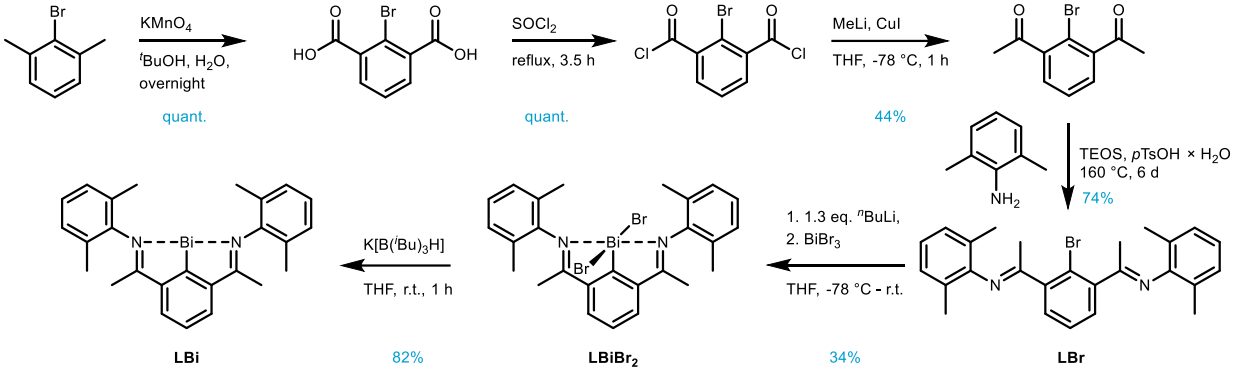
UV-Vis absorption spectra were recorded on a TIDAS fiber optic diode array spectrometer, which consists of a combination of MCS UV/Vis and PGS NIR instruments from *j&m Analytic* AG. Extinction coefficients were measured using quartz cells with an optical path length of 1 cm, which were purchased from *Hellma Analytics*, or in a custom-built quartz cuvette with vacuum valve, whereby the original cuvette was a 1 cm cell with a 221.01Qs tube purchased from *Hellma Analytics.*

Photoluminescence Spectroscopy Excitation and emission spectra and the respective lifetimes of the excited states were recorded with the FluoTime 300 spectrometer from *PicoQuant*. All measurements were performed in dry 2-Me-THF, THF or CH_2Cl_2. Spectra of **$LBiBr_2$** in 2-MeTHF were recorded in quartz tubes. Solutions of **LBi** in 2-MeTHF were handled in custom-built 5 mm boroeco 5-7 NMR tubes fitted with a J .YOUNG`s Teflon cap and an insert. Spectra of **LBi** in THF were subjected to four freeze-pump-thaw cycles prior to measurement to ensure that no quenching through residual O_2 could take place, and subsequently sealed in the cuvettes by melting. UV-vis absorption spectra were recorded prior to and after measurements and subsequently compared to guarantee no degradation during the measurement. Absolute quantum yields were determined using an integrating sphere within the FluoTime 300 spectrometer.

Single Crystal X-ray Diffraction for **LBiBr$_2$** and **LBr** was conducted on a STOE IPDS II diffractometer from *STOE & Cie GmbH* at 100 K equipped with a graphite monochromator and a Mo K_α-radiation source (λ = 0.71073 Å). The X-Area program package was used for data processing, and absorption correction was conducted both semi-empirically and spherically. The structure was solved with SHELXT[1, 2] and the OLEX2[3] program packages. All non-hydrogen atoms were refined anisotropically. Intermolecular interactions were analyzed using the Mercury and OLEX2 program packages. Deposition Numbers 2394890 and 2412557 contain the supplementary crystallographic data for this paper.

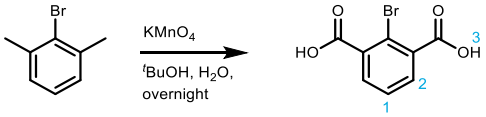
Quantum chemical calculations based on density functional theory (DFT) employed the Gaussian 16 program package.[4] Geometry optimization was followed by vibrational analysis. All calculations were performed in either CH_2Cl_2 for **LBiBr$_2$** or benzene for **LBi** as the solvent, applying the polarizable continuum model (SMD).[5] Electronic spectra were calculated at the optimized ground-state structures by the time-dependent-DFT method. In conjunction with the Perdew, Burke Enzerhof exchange and correlation functional PBE0,[6, 7] the fully realistic small-core multiconfiguration Dirac-Hartree Fock-adjusted pseudopotential and the corresponding set for Bi(ECP60MDF)[8] and 6-31(G)[9] polarizable double-ζ basis sets for the remaining atoms were used. ORCA Calculations including spin−orbit coupling were carried out using the ORCA 5.0.4 software package.[10] For the ground and excited triplet states, the optimization was performed according to the unrestricted Kohn−Sham (KS) DFT process. LR-CPCM was used for calculations of dissolved species **LBiBr$_2$** or **LBi**, using CH_2Cl_2 or benzene. For the excited states, TD-DFT without TDA was employed. Optimized structures were checked for negative frequencies. The spin−orbit integrals were calculated using the RI-SOMF(1X) approximation.[11] Calculations were done using the PBE0-functional (PBE0)[6, 7] with the SARC-ZORA-TZVP basis set[12-14] for Bi and the ZORA-def2-TZVP basis[15, 16] and the SARC/J decontracted def2/J auxiliary basis for all other elements. The GaussSum,[17] Avogadro,[18] GNU Parallel[19] and vmd[20] program packages were used in combination with POV-Ray[21] for data processing and graphical representations.

3. Synthesis



Scheme S1. Schematic overview of the synthesis steps conducted in this work. All syntheses were conducted based on modified literature procedures.

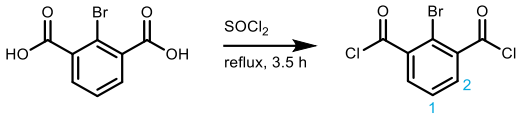
2-Bromoisophthalic acid[22]



2-Bromo-*m*-xylene (18.0 mL, 131 mmol, 1.00 eq.) was suspended in a ^{t}BuOH/H_2O mixture (135 mL/250 mL) and heated to reflux at 110 °C. KMnO4 (128 g, 810 mmol, 6.18 eq.) was added in portions and the mixture was stirred for 14 h at 110 °C and then allowed to cool to room temperature. The resulting mixture was filtered through a Büchner funnel. The black precipitate was extracted with distilled water (3 x 40 mL). The combined organic/aqueous phases were acidified with concentrated aqueous HCl (10 mL, 37m%), resulting in the precipitation of a white solid which was collected by Büchner filtration. The white solid was dried in a vacuum desiccator over P_2O_5 for four days to remove residual traces of water. 2-Bromoisophthalic acid (32.0 g, 131 mmol) was obtained as a white, fluffy solid in quantitative yield.

^{1}H-NMR (400 MHz, 298 K, DMSO-d_6) δ [ppm] = 13.59 (s, 1H, H-3), 7.69 (d, $^{3}J_{HH}$ = 7.6 Hz, 2H, H-2), 7.52 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H, H-1).

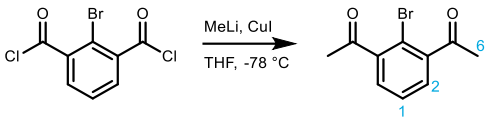
2-Bromoisophthhaloyl dichloride[22]



Under inert gas conditions, 2-bromoisophtalic acid (4.03 g, 16.5 mmol, 1.00 eq.) was suspended in $SOCl_2$ (30 mL). The reaction mixture was heated to reflux at 100 °C for 2.5 h and then at 120 °C for an additional hour until the 2-bromoisophthalic acid had dissolved completely, resulting in a clear yellow solution. After cooling to room temperature, $SOCl_2$ was removed *in vacuo*. 2-Bromoisophthaloyl dichloride (4.64 g, 16.5 mmol) was obtained as white solid in quantitative yield.

^{1}H-NMR (500 MHz, 298 K, $CDCl_3$) δ [ppm] = 7.99 (d, $^{3}J_{HH}$ = 7.9 Hz, 2H, H-2), 7.61 (t, $^{3}J_{HH}$ = 7.9 Hz, 1H, H-1).

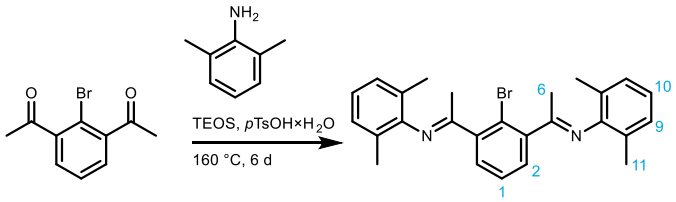
2,6-Diacetylbromobenzene[22]



Under inert gas conditions, CuI (5.31 g, 27.9 mmol, 2.16 eq.) was suspended in dry THF (200 mL) and the suspension was cooled to -78 °C. A solution of MeLi·LiBr in dry Et_2O (37 mL, 1.50 M, 4.30 eq.) was added. This suspension was stirred at - 78 °C for one hour. A solution of 2-bromoisophthaloyl dichloride (3.64 g, 12.9 mmol, 1.00 eq.) in THF (24 mL, dry) was added dropwise to the reaction mixture. The resulting bright yellow solution was stirred at -78 °C for three hours and then slowly warmed to room temperature overnight, resulting in a black reaction mixture, which was quenched with ^{i}PrOH (10 mL). The solvent was removed under reduced pressure. Aqueous HCl (50 mL, 1.0 M) was added to the residue and the resulting grey solid was removed by Büchner filtration. The precipitate was extracted with Et_2O (2 x 50 mL). The aqueous and organic phases were separated and the aqueous phase extracted with Et_2O (2 x 50 mL). The combined yellow organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was obtained as a brown oil, which was purified by column chromatography on silica (PE/EE, v/v, 5:1). 2,6-Diacetylbromobenzene (1.37 g, 5.7 mmol) was obtained as a pale-yellow oil in 44% yield.

^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) δ [ppm] = 7.50-7.36 (m, 3H, H-2, H-1), 2.62 (s, 6H, H-6).

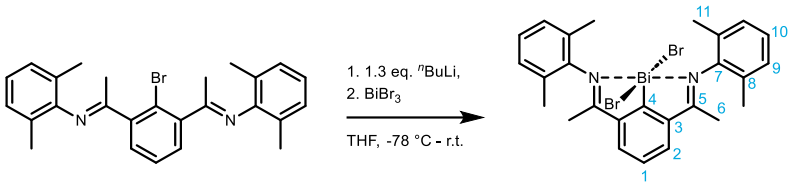
(1E,1'E)-1,1'-(2-Bromo-1,3-phenylene)bis(N-(2,6-dimethylphenyl)ethan-1-imine) LBr[22]



Under inert gas conditions, 2,6-diacetylbromobenzene (1.27 g, 5.3 mmol, 1.00 eq.), 2,6-dimethylaniline (2.0 mL, 16.1 mmol, 3.05 eq.), $Si(OEt)_4$ (9.4 mL, 42 mmol, 8.0 eq.) and *p*-toluene sulfonic acid monohydrate (512 mg, 2.7 mmol, 0.51 eq.) were placed into a Schlenk tube and stirred at 160 °C for six days. The dark brown reaction mixture was quenched by addition of aqueous NaOH (20 mL, 0.10 M) and EtOH (14 mL). The resulting deep violet organic phase was separated and concentrated under reduced pressure. Distilled water (25 mL) was added and the aqueous solution was extracted with Et_2O (4 x 50 mL). The combined brown organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica (PE/EE, v/v, 5:1). (1E,1'E)-1,1'-(2-Bromo-1,3-phenylene)bis(N-(2,6-dimethylphenyl)ethan-1-imine) (**LBr**) (1.75 g, 3.91 mmol) was obtained as a beige solid in 74% yield. Single crystals suitable for SC-XRD were obtained by recrystallization from ^{n}heptane.

^{1}H-NMR (400 MHz, 298 K, $CDCl_3$) δ [ppm] = 7.52-7.47 (m, 3H, H-1 & H-2), 7.08 (d, $^3J_{HH}$ = 7.6 Hz, 4H, H-9), 6.96 (t, $^3J_{HH}$ = 7.6 Hz, 2H, H-10), 2.21 (s, 12H, H-11), 2.08 (s, 6H, H-6).

LBiBr$_2$[23]



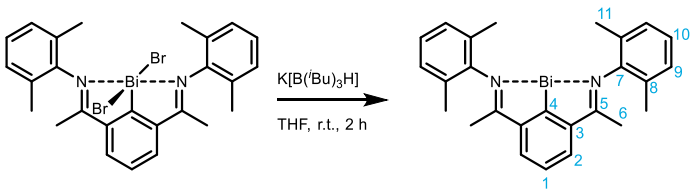
Under inert gas conditions, ^{n}butyllithium (0.45 mL, 2.5 M in hexane, 1.13 µmol, 1.30 eq.) was added dropwise to a stirred solution of **LBr** (390 mg, 872 µmol, 1.00 eq.) in THF (30 mL, dry) at -78 °C. The mixture was stirred at -78 °C for one hour. The resulting brown solution was added dropwise over the course of 45 minutes to a pre-cooled (-78 °C) solution of $BiBr_3$ (391 mg, 871 µmol, 1.00 eq.) in THF (15 mL, dry), under vigorous stirring. The turquoise solution was allowed to warm to room temperature overnight, yielding a yellow-green suspension. The solvent was removed under reduced pressure and the residue was washed with a mixture of hexane/Et_2O (3:1, v/v, 2 x 40 mL). The light brown residue was extracted with CH_2Cl_2 (2 x 40 mL), yielding a bright yellow solution. The solvent was removed under reduced pressure, yielding **LBiBr$_2$** (220 mg, 299 mmol) as a pale-yellow solid in 34% yield. Single crystals suitable for SC-XRD were obtained by evaporation of a concentrated solution of **LBiBr$_2$** in dichloromethane.

^{1}H-NMR (600 MHz, 298 K, CD_2Cl_2) δ [ppm] = 8.65 (d, $^3J_{HH}$ =7.8 Hz, 2H, H-2), 8.08 (t, $^3J_{HH}$ =7.8 Hz, 1H, H-1), 7.23-7.15 (m, 6H, H-9, H-10), 2.42 (s, 6H, H-6), 2.41 (s, 12H, H-11).

^{13}C-NMR (151 MHz, 298 K, CD_2Cl_2) δ [ppm] = 209.0 (C-4), 181.8 (C-5), 148.3 (C-3), 144.7 (C-7), 137.7 (C-2), 131.1 (C-8), 129.7 (C-1), 129.2 (C-9), 126.9 (C-10), 20.9 (C-11), 19.9 (C-6).

Elemental Analysis calculated for $C_{26}H_{27}BiBr_2N_2$: 42.41% C, 3.70% H, 3.80% N; found: 42.57% C, 4.10% H, 3.82% N.

LBi[23]



Under inert gas conditions at room temperature, a solution of K[B(^{t}Bu)$_3$H] (0.46 mL, 1.0 M in THF, 459 µmol, 2.00 eq.) was added dropwise to a vigorously stirred solution of **LBiBr$_2$** (169 mg, 229 µmol, 1.00 eq.) in THF (20 mL, dry), resulting in a deep green solution. After stirring for one hour at room temperature, the solvent was removed *in vacuo*, and the Schlenk flask was transferred to a nitrogen-filled glovebox for the workup. The dark green residue was extracted six times with dry ^{n}hexane (6 mL each) until the ^{n}hexane extract was colourless. The solvent was allowed to evaporate over the course of three days, leading to dark green, (micro)crystalline **LBi** (109 mg, 189 µmol) in 82% yield.

^{1}H-NMR (400 Hz, 298 K, C_6D_6) δ [ppm] = 8.09 (d, $^3J_{HH}$ = 7.6 Hz, 2H, H-2), 7.11 (t, $^3J_{HH}$ = 7.2 Hz, 1H, H-1), 7.02 (d, $^3J_{HH}$ = 7.5 Hz, 4H, H-9), 6.90 (t, $^3J_{HH}$ = 8.1, 6.9 Hz, 2H, H-10), 2.48 (s, 6H, H-6), 2.02 (s, 12H, H-11).

^{13}C-NMR (101 Hz, 298 K, C_6D_6) δ [ppm] = 203.8 (C-4), 171.7 (C-5), 147.8 (C-8), 146.1 (C-3), 133.2 (C-2), 129.0 (C-9), 128.1 (C-7) 124.7 (C-10), 121.8 (C-1), 19.2 (C-11), 17.7 (C-5).

4. NMR Spectroscopy

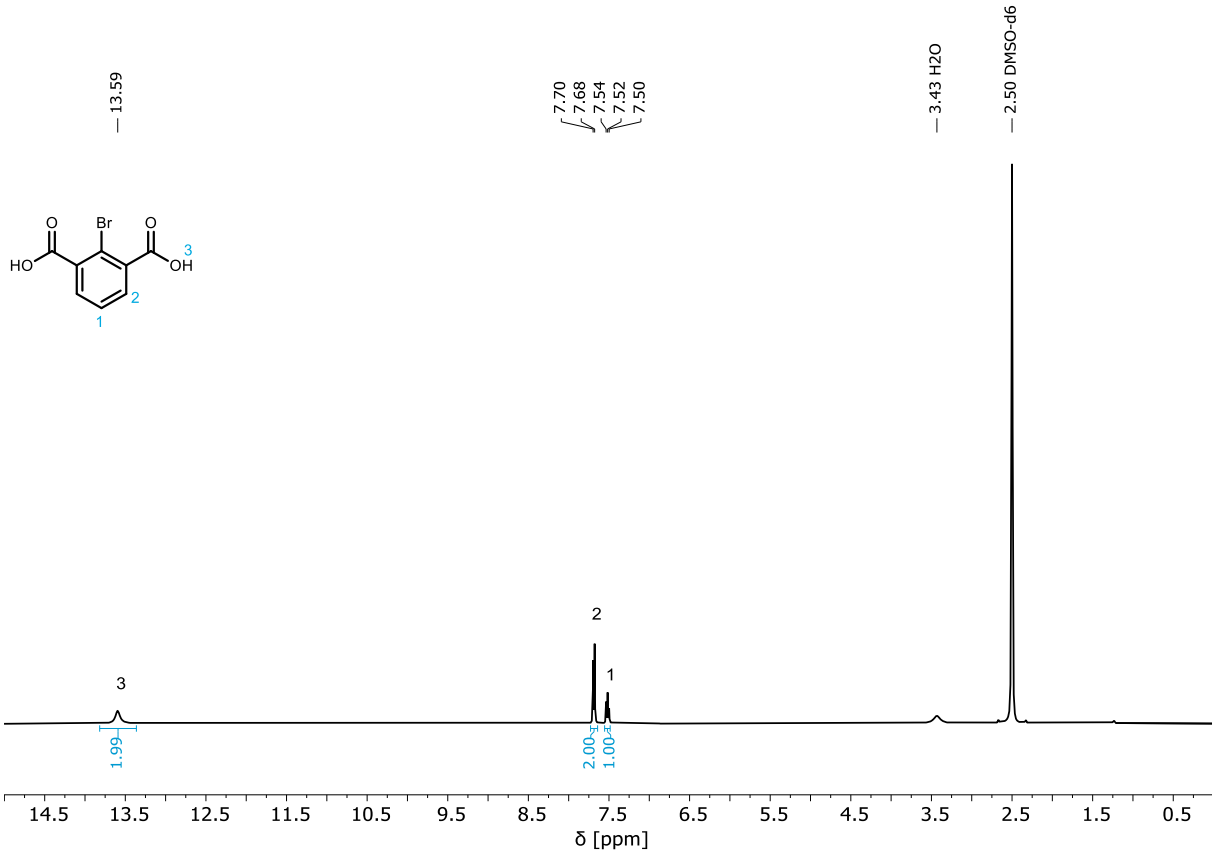


Figure S1. ^{1}H-NMR spectrum of 2-bromoisophthalic acid in DMSO-d^{6} at 298 K.

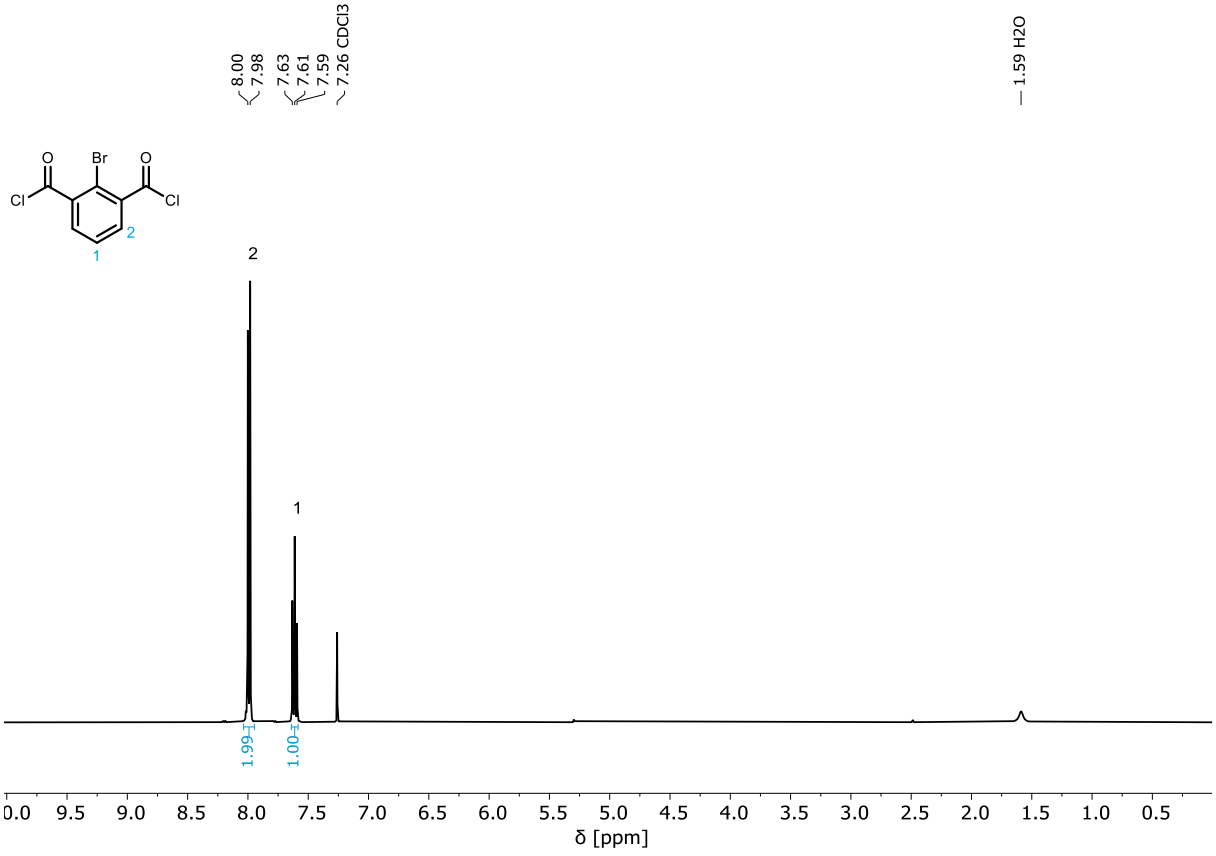


Figure S2. ^{1}H-NMR spectrum 2-bromoisophthhaloyl dichloride in $CDCl_3$ at 298 K.

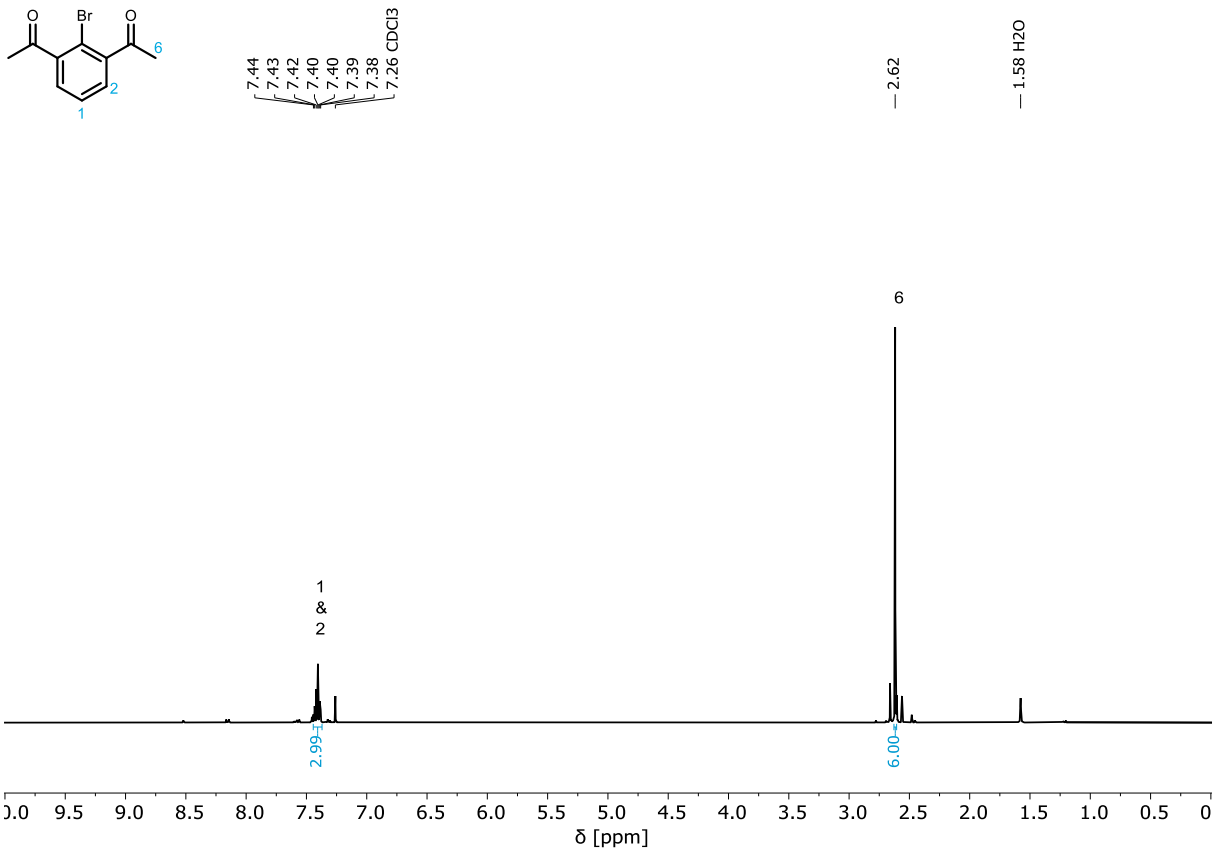


Figure S3. ^{1}H-NMR spectrum of 2,6-diacetylbromobenzene in $CDCl_3$ at 298 K.

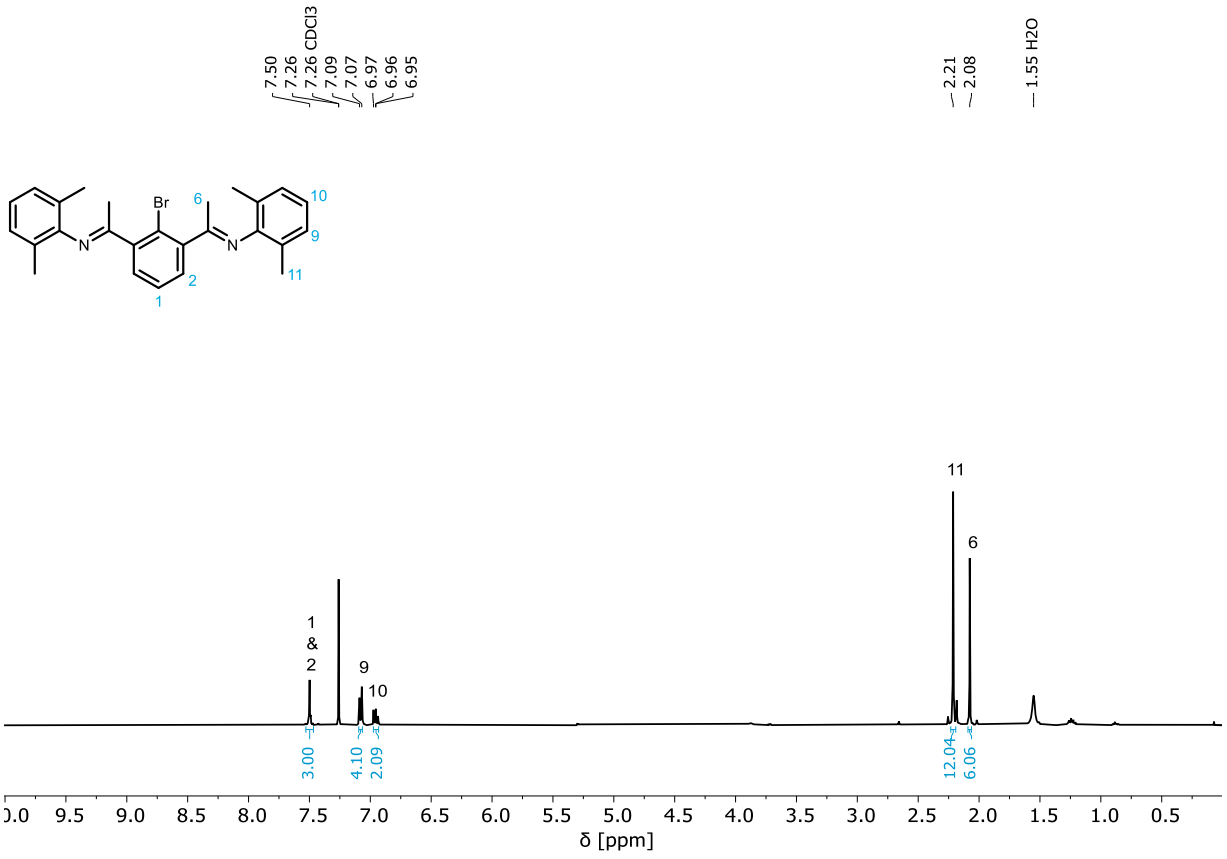


Figure S4. ^{1}H-NMR spectrum of **LBr** in $CDCl_3$ at 298 K.

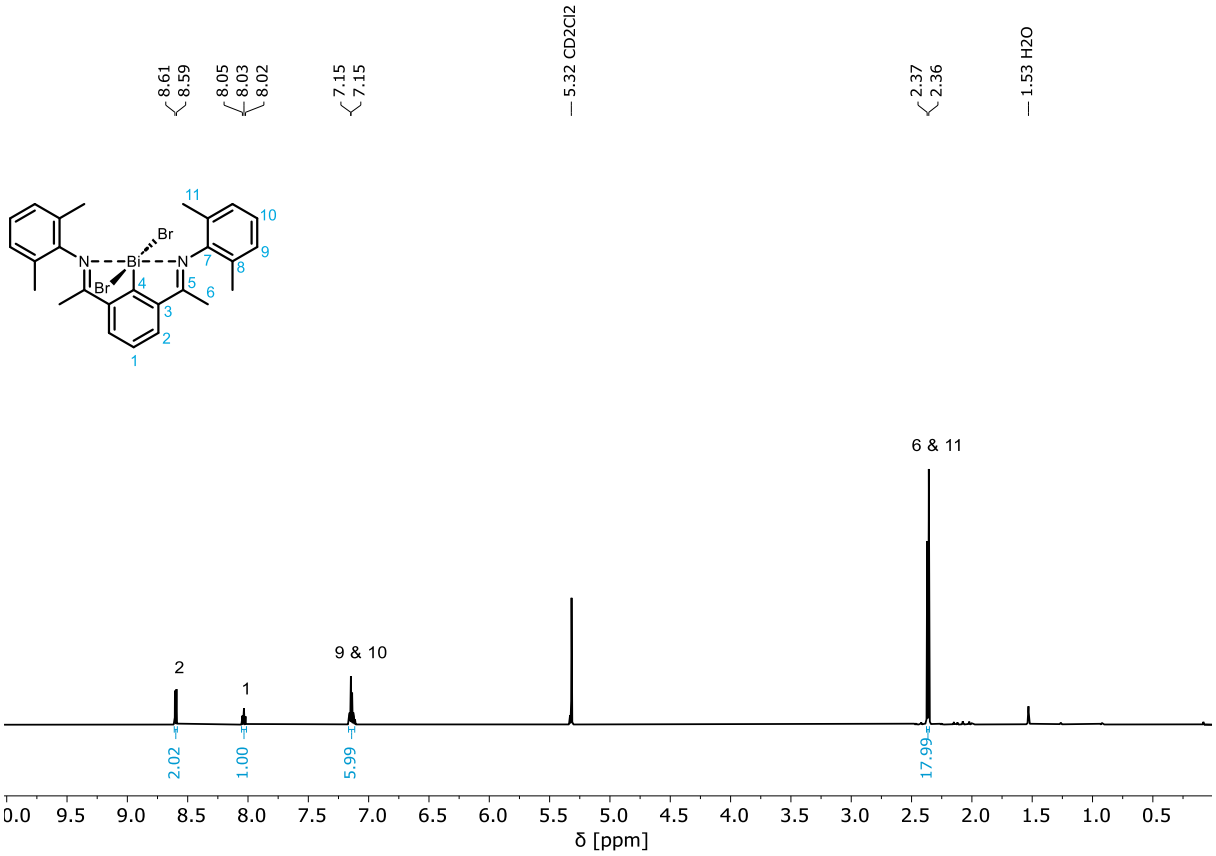


Figure S5. ^{1}H-NMR spectrum of **LBiBr$_2$** in CD_2Cl_2 at 298 K.

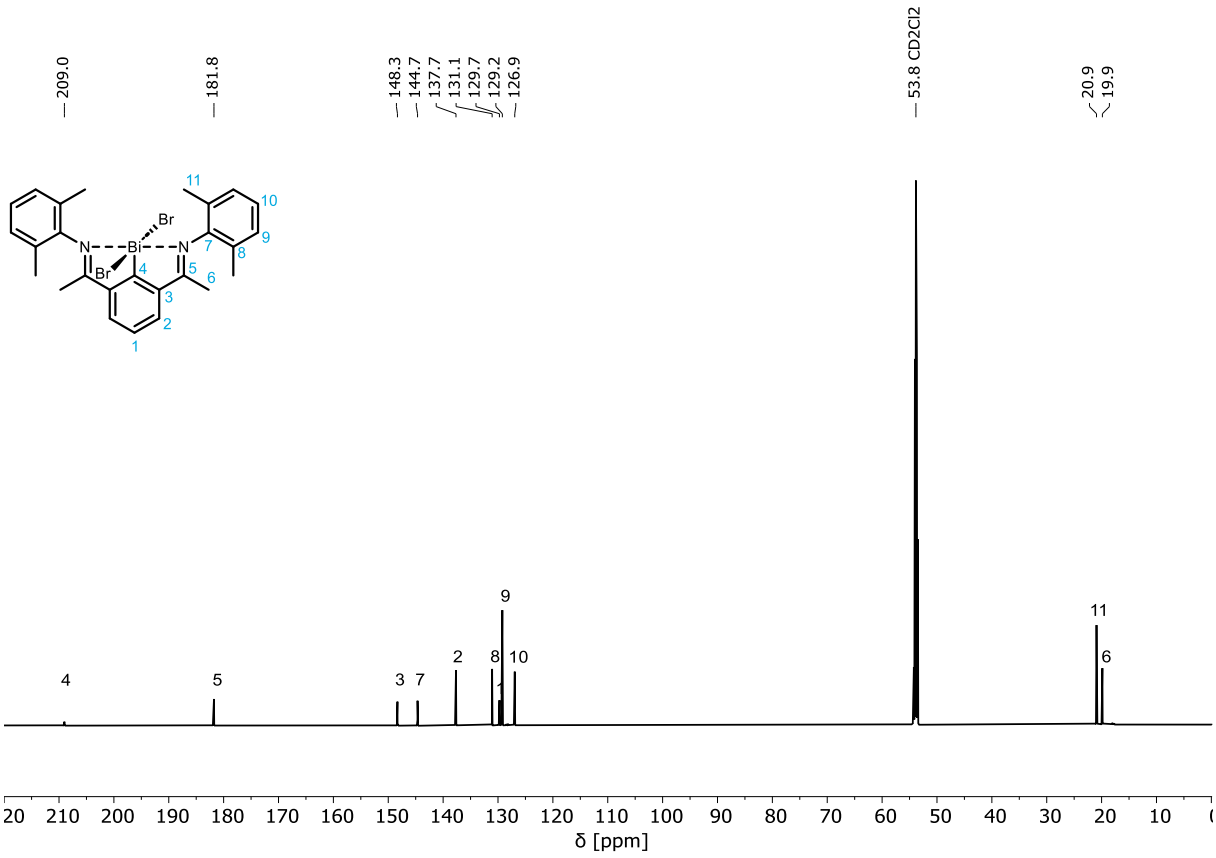


Figure S6. ^{13}C{^{1}H}-NMR spectrum of **LBiBr$_2$** in CD_2Cl_2 at 298 K.

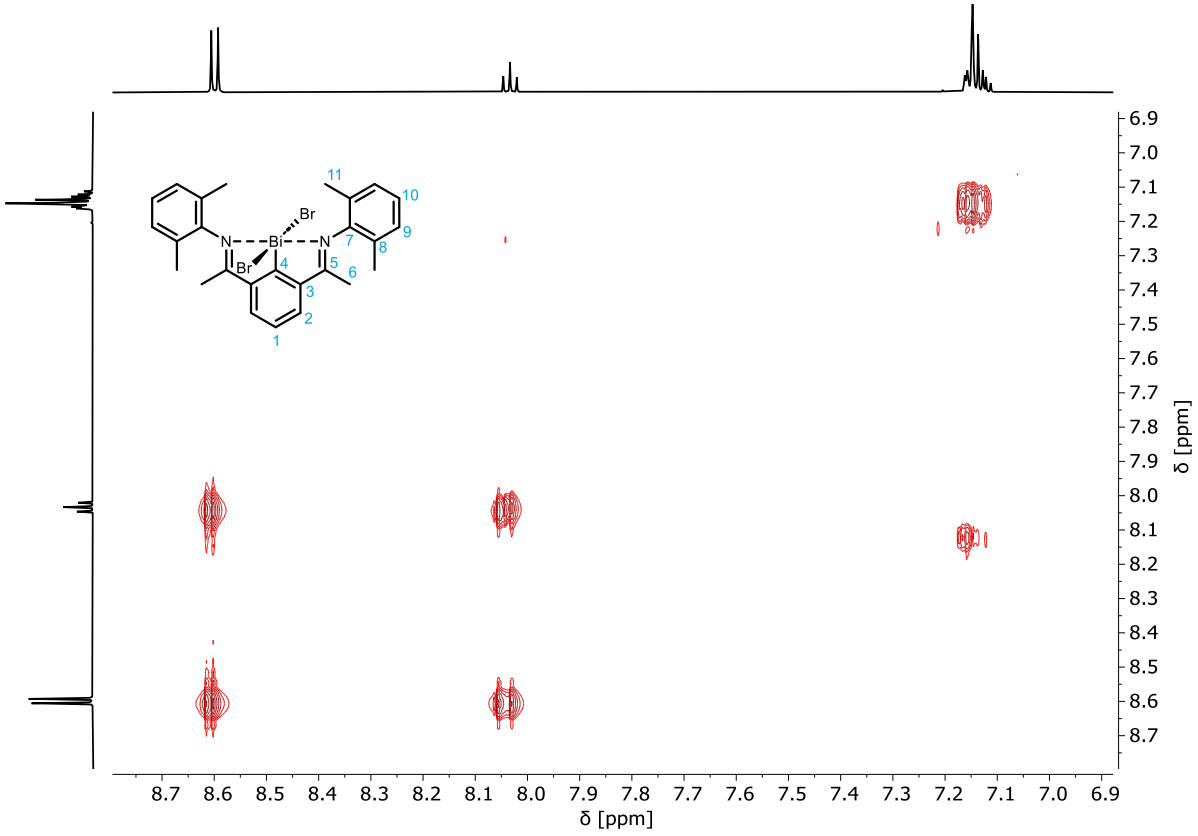


Figure S7. ^{1}H-NMR COSY spectrum of **LBiBr$_2$** in CD_2Cl_2 at 298 K.

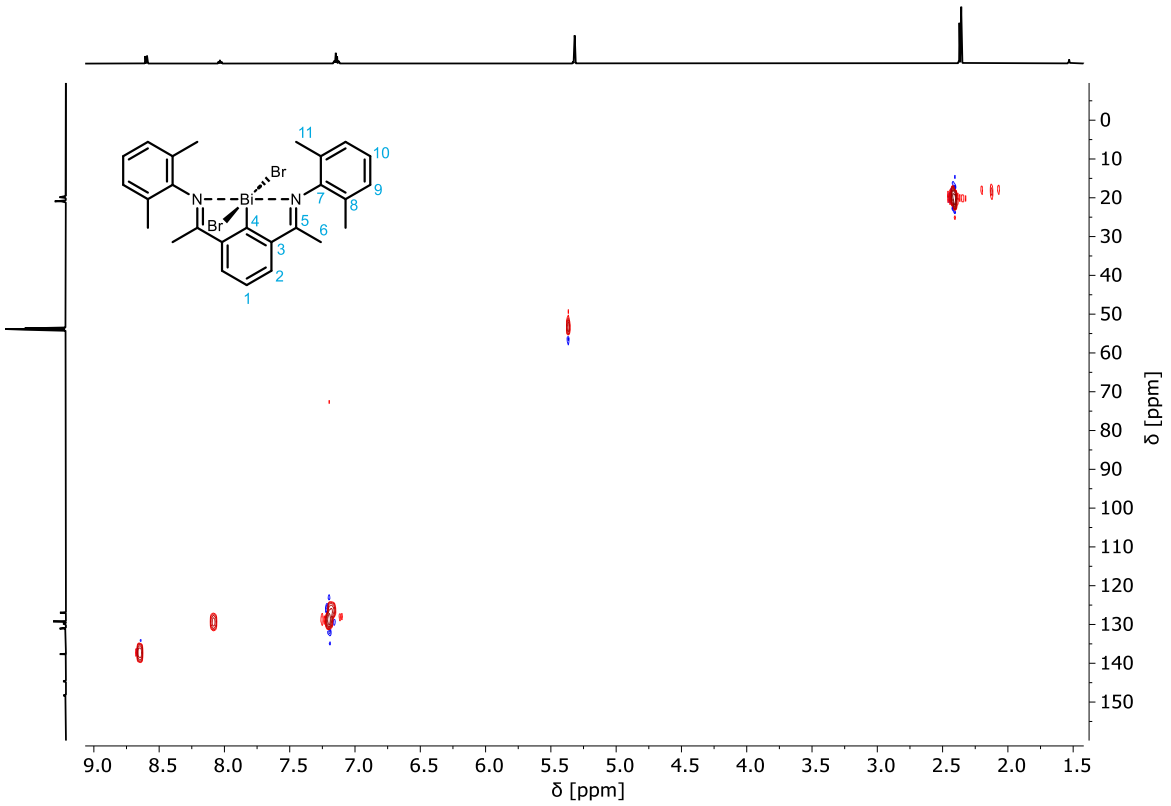


Figure S8. ^{1}H-NMR/^{13}C{^{1}H}-NMR HSQC spectrum of **LBiBr$_2$** in CD_2Cl_2 at 298 K.

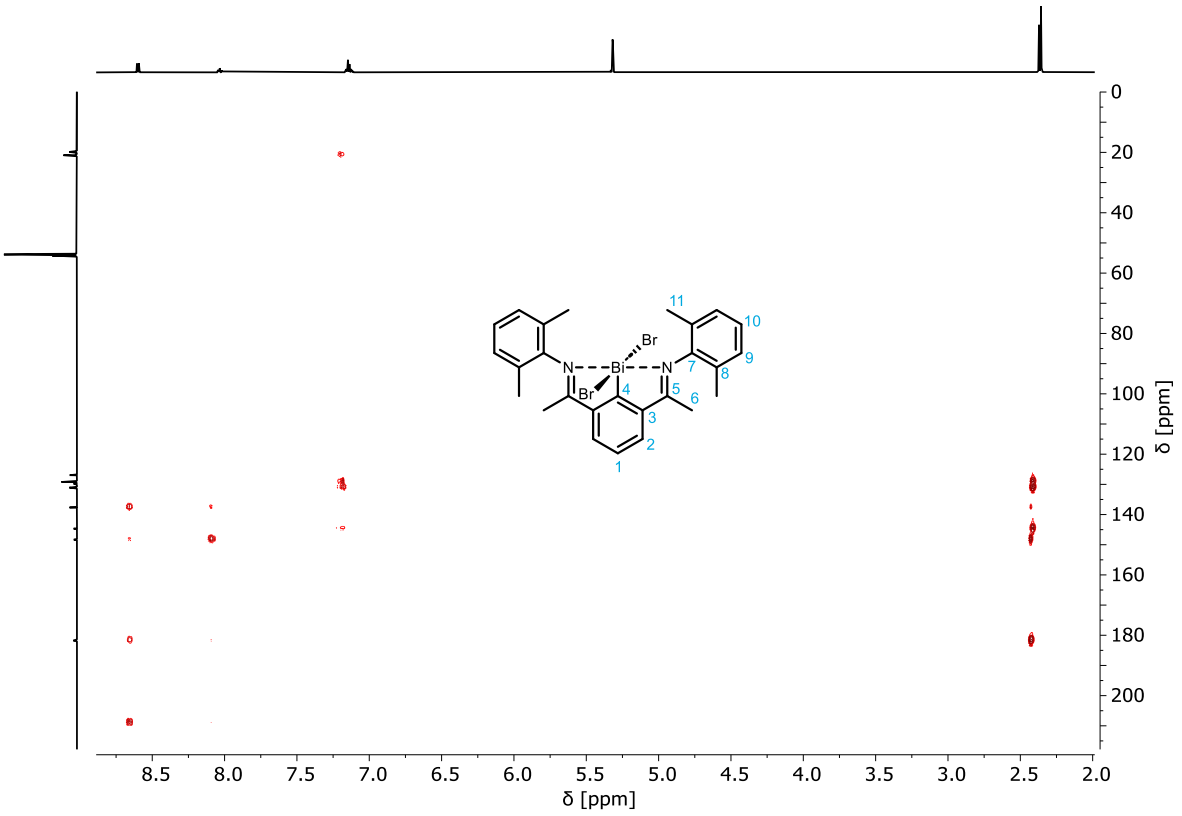


Figure S9. ^{1}H-NMR/^{13}C{^{1}H}-NMR HMBC spectrum of **LBiBr$_2$** in CD_2Cl_2 at 298 K.

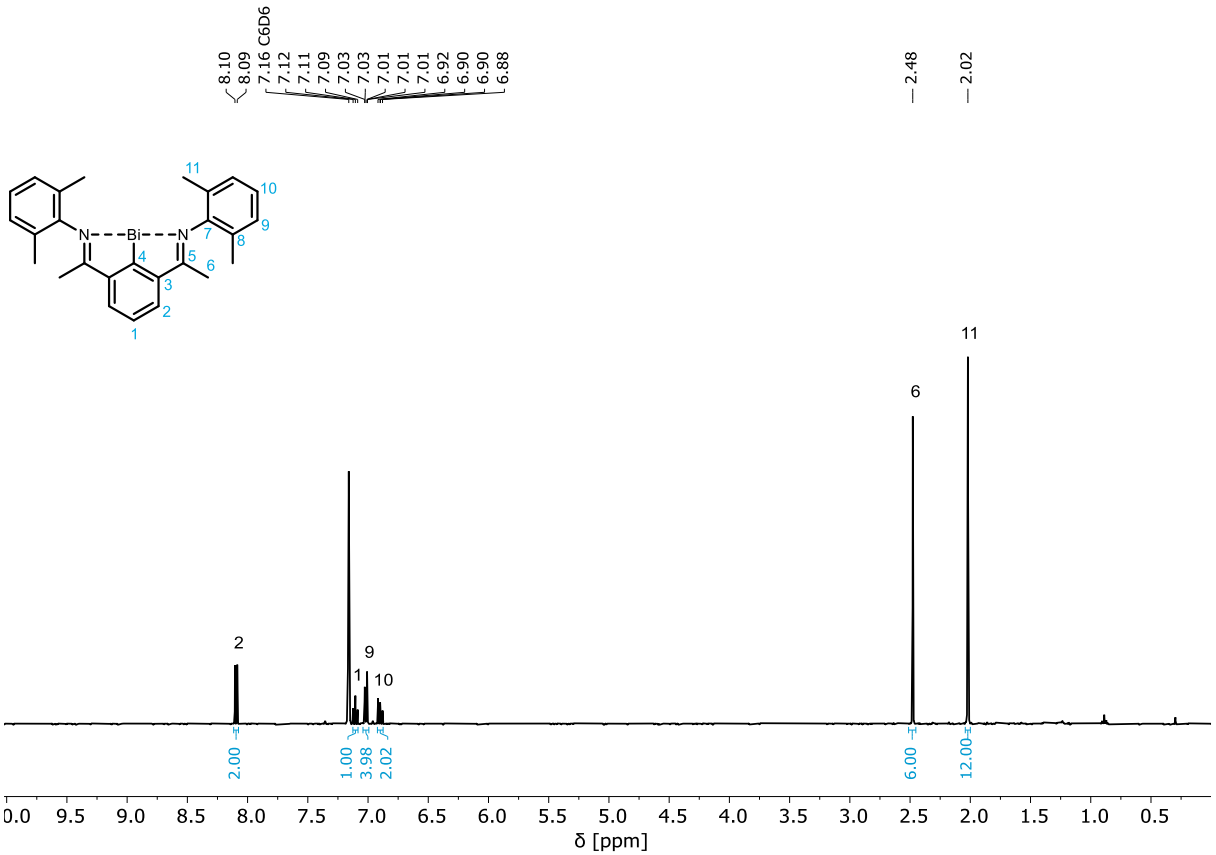


Figure S10. ^{1}H-NMR spectrum of **LBi** in C_6D_6 at 298 K.

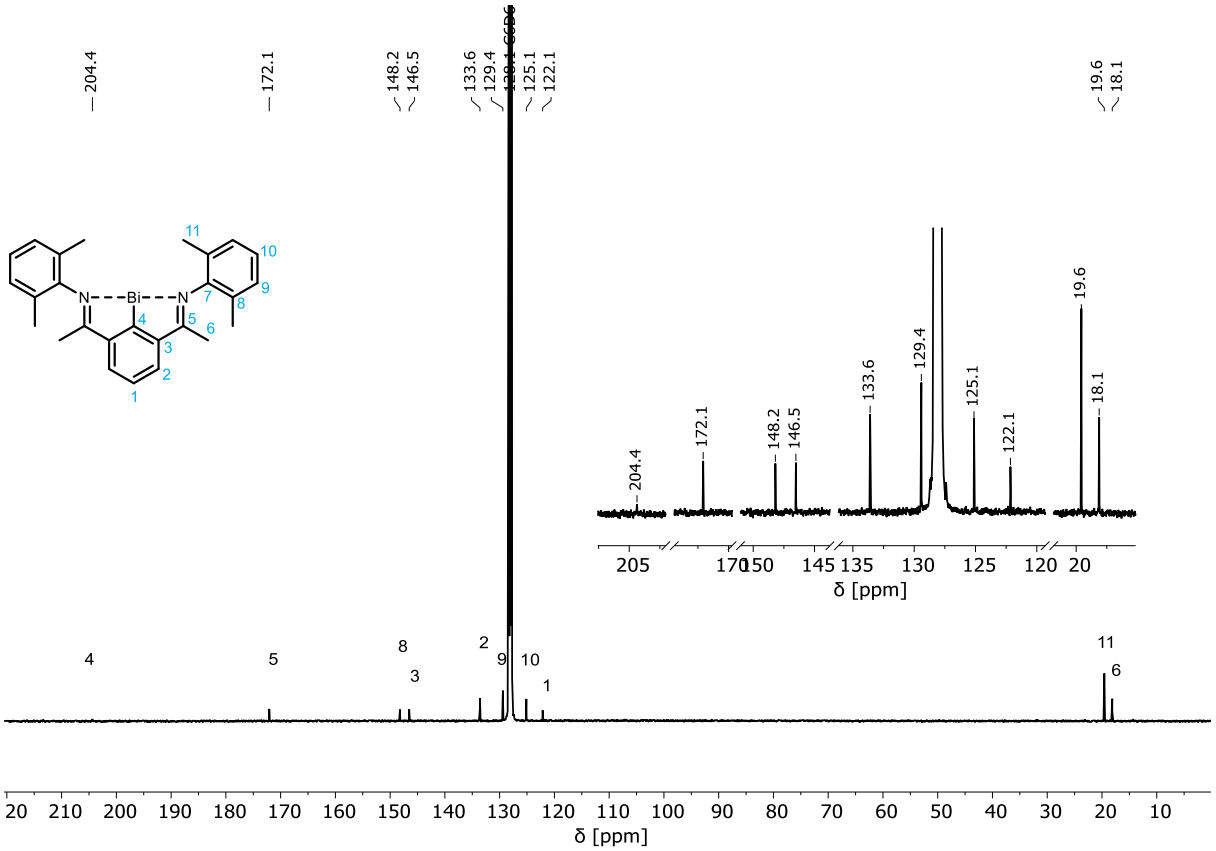


Figure S11. $^{13}C\{^{1}H\}$-NMR spectrum of **LBi** in C_6D_6 at 298 K.

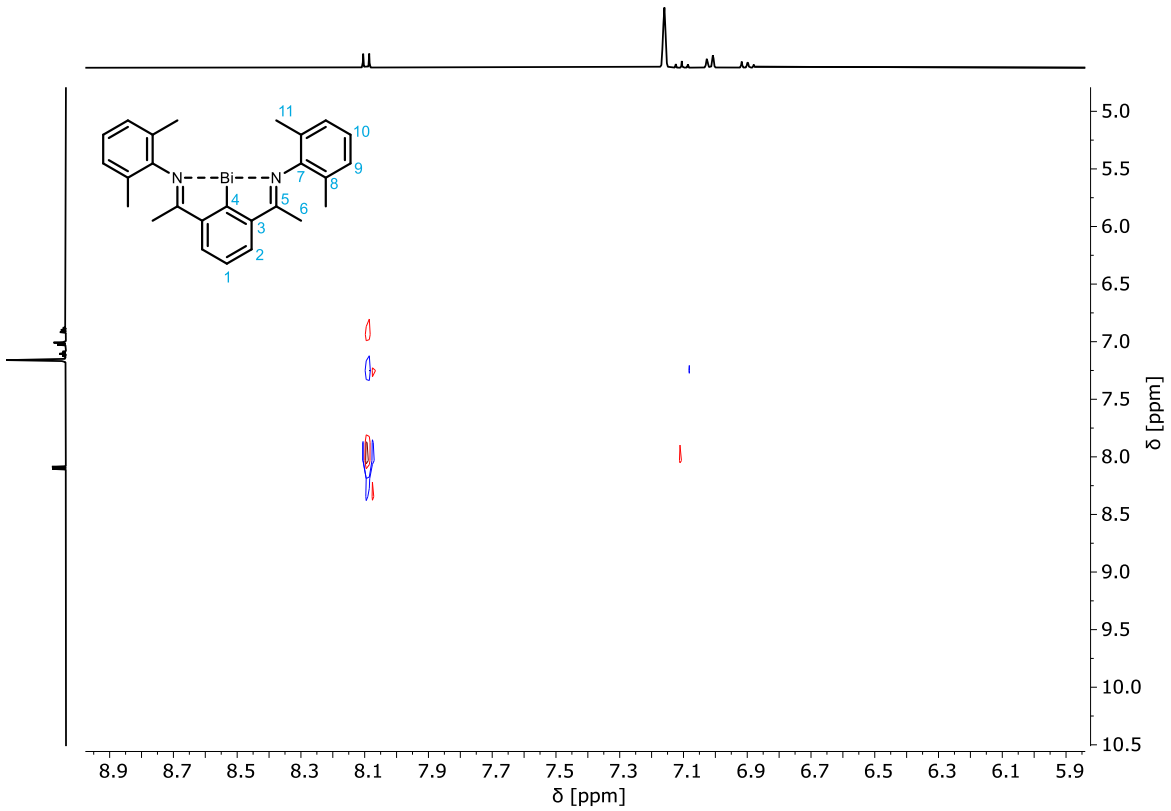


Figure S12. ^{1}H-NMR COSY spectrum of **LBi** in C_6D_6 at 298 K.

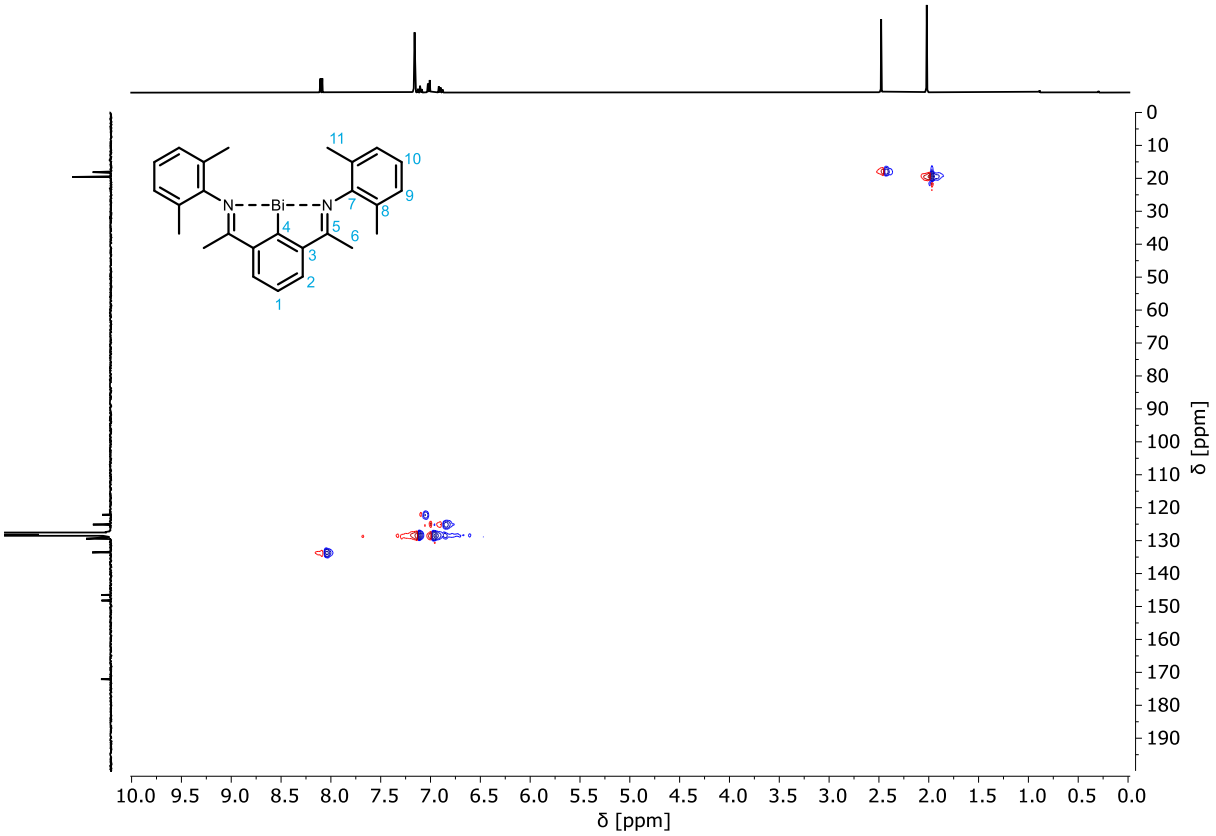


Figure S13. ^{1}H-NMR/^{13}C{^{1}H}-NMR HSQC spectrum of **LBi** in C_6D_6 at 298 K.

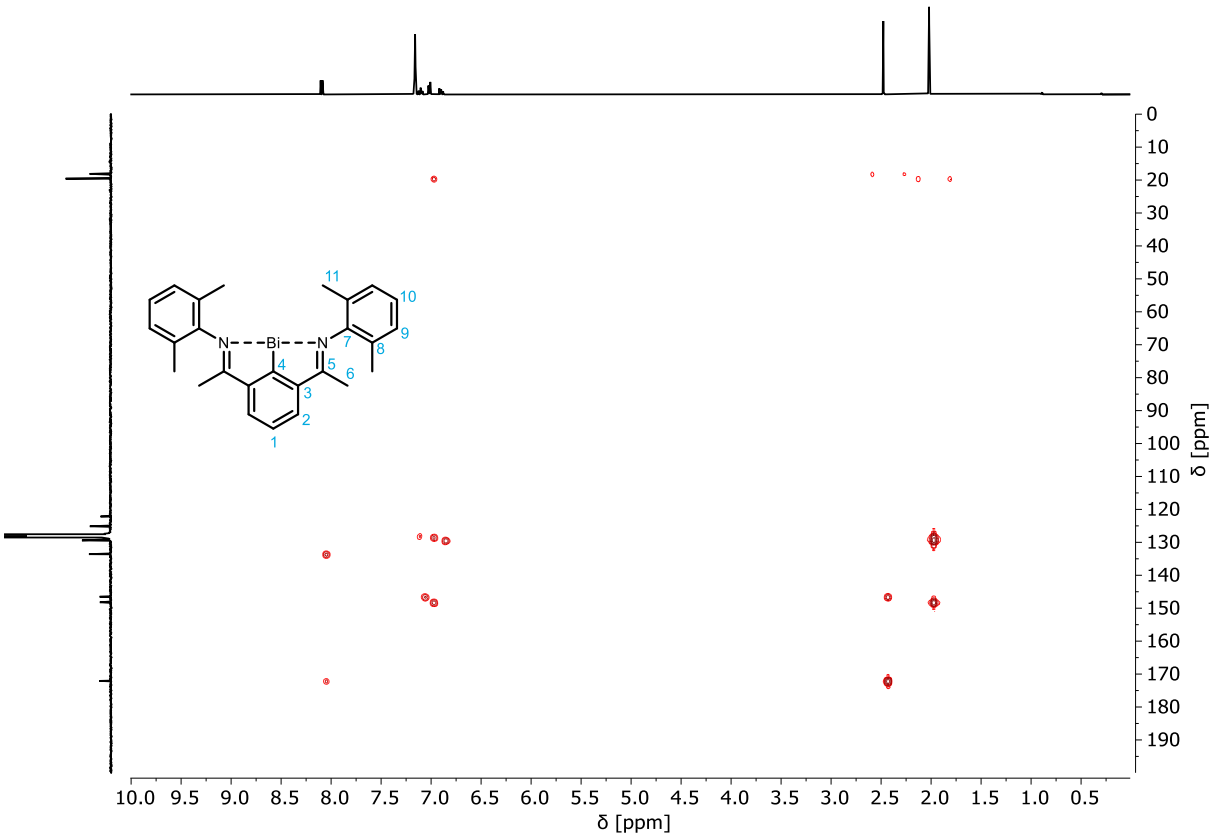


Figure S14. ^{1}H-NMR/^{13}C{^{1}H}-NMR HMBC spectrum of **LBi** in C_6D_6 at 298 K.

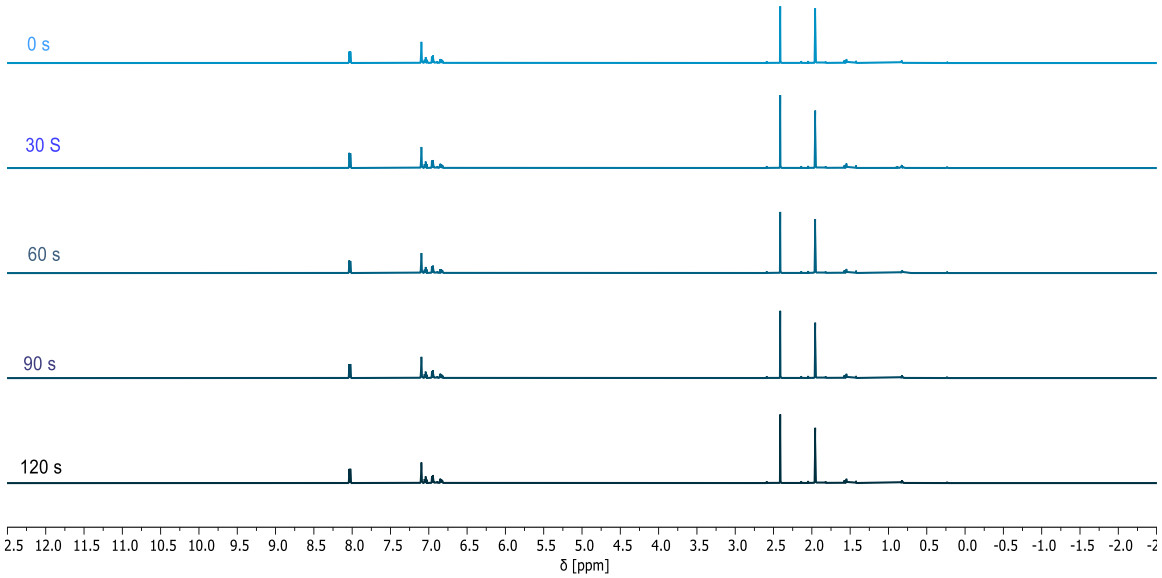


Figure S16. Photostability tests on **LBi** in C_6H_6 at r.t. after irradiation at λ = 365 nm (2.4 W).

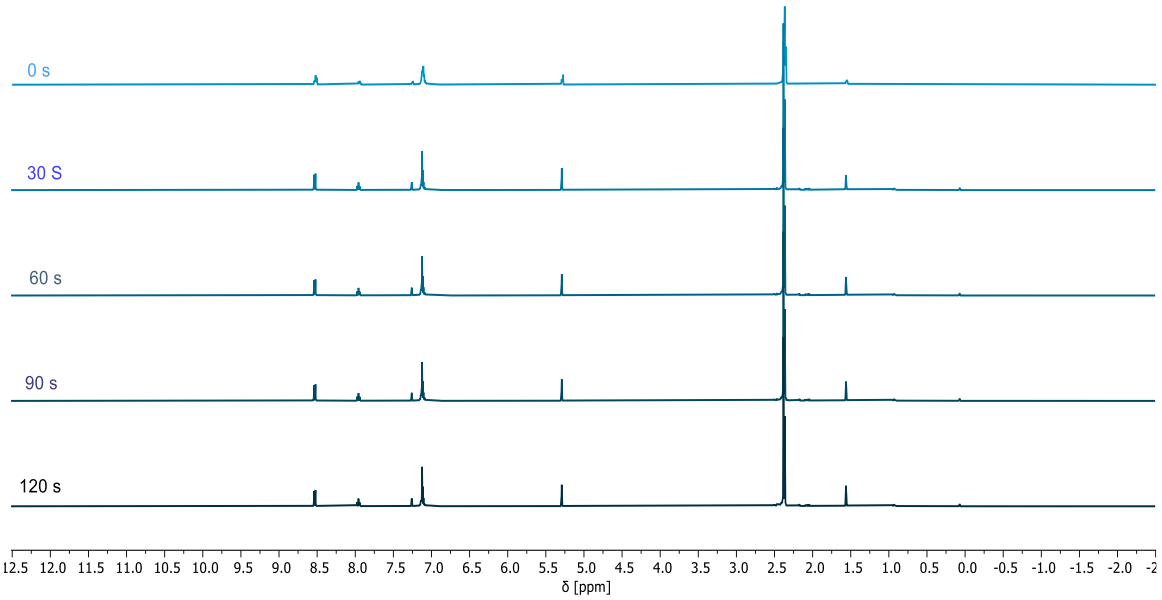


Figure S15. Photostability tests on **$LBiBr_2$** in CD_2Cl_2 at r.t. after irradiation at λ = 365 nm (2.4 W).

5. SC-XRD

Table S1: Crystal data and structure refinement for **$LBiBr_2$**.

Identification code	KD109-NMR
Empirical formula	$C_{26.25}H_{27.5}BiBr_2Cl_{0.5}N_2$
Formula weight	757.53
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.2163(6)
b/Å	8.2052(2)
c/Å	28.5094(12)
α/°	90
β/°	96.531(4)
γ/°	90
Volume/Å^3	3071.6(2)
Z	4
ρ_{calc}g/cm^3	1.638
μ/mm^{-1}	8.399
F(000)	1442.0
Crystal size/mm^3	0.5 × 0.183 × 0.01
Radiation	Mo K_α (λ = 0.71073)
2Θ range for data collection/°	5.02 to 53
Index ranges	$-16 \le h \le 16$, $-10 \le k \le 9$, $-35 \le l \le 35$
Reflections collected	13046
Independent reflections	6242 [R_{int} = 0.0460, R_{sigma} = 0.0444]
Data/restraints/parameters	6242/0/286
Goodness-of-fit on F^2	1.068
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0489, wR_2 = 0.1319
Final R indexes [all data]	R_1 = 0.0640, wR_2 = 0.1454
Largest diff. peak/hole / e Å^{-3}	2.17/-2.44

Table S2. Bond lengths in the solid-state structure of **$LBiBr_2$**.

Atom1	Atom2	Length [Å]	Atom1	Atom2	Length [Å]	Atom1	Atom2	Length [Å]
Bi1	Br2	2.9115	C21	C22	1.4058	C25	C24	1.3662
Bi1	Br1	2.7577	C3	C2	1.3959	C25	C26	1.4866
Bi1	N1	2.4704	C15	H15	0.9299	C14	H14a	0.96
Bi1	N2	2.4543	C15	C16	1.3923	C14	H14b	0.9601
Bi1	C4	2.195	C2	H2	0.9301	C14	H14c	0.9601
N1	C5	1.3073	C7	C12	1.4148	C14	C8	1.5114
N1	C7	1.4259	C7	C8	1.3999	C24	H24	0.93
N2	C20	1.4496	C12	C13	1.5047	C24	C23	1.3813
N2	C18	1.2827	C12	C11	1.3872	C11	H11	0.9299
C4	C3	1.3742	C16	C18	1.4805	C11	C10	1.3925
C4	C16	1.4173	C19	H19a	0.9601	C8	C9	1.382
C5	C3	1.5	C19	H19b	0.96	C22	H22	0.93
C5	C6	1.4811	C19	H19c	0.9599	C22	C23	1.3636
C27	H27a	0.9599	C19	C18	1.4865	C9	H9	0.93
C27	H27b	0.9601	C6	H6a	0.96	C9	C10	1.4038
C27	H27c	0.9599	C6	H6b	0.96	C26	H26a	0.9601
C27	C21	1.5036	C6	H6c	0.9599	C26	H26b	0.96
C1	H1	0.9299	C20	C25	1.4295	C26	H26c	0.9598
C1	C15	1.3704	C13	H13a	0.96	C23	H23	0.93
C1	C2	1.3733	C13	H13b	0.9601	C10	H10	0.9301
C21	C20	1.4015	C13	H13c	0.9599			

Table S3. Angles in the solid-state structure of **LBiBr$_2$**.

Atom1	Atom2	Atom3	Angle [°]	Atom1	Atom2	Atom3	Angle [°]
Br2	Bi1	Br1	168.35	H19b	C19	H19c	109.47
Br2	Bi1	N1	92.08	H19b	C19	C18	109.47
Br2	Bi1	N2	89.29	H19c	C19	C18	109.47
Br2	Bi1	C4	79.05	C5	C6	H6a	109.46
Br1	Bi1	N1	84.91	C5	C6	H6b	109.47
Br1	Bi1	N2	86.26	C5	C6	H6c	109.48
Br1	Bi1	C4	89.34	H6a	C6	H6b	109.47
N1	Bi1	N2	142.16	H6a	C6	H6c	109.47
N1	Bi1	C4	71.19	H6b	C6	H6c	109.48
N2	Bi1	C4	71.98	N2	C20	C21	118.35
Bi1	N1	C5	114.43	N2	C20	C25	119.71
Bi1	N1	C7	121.84	C21	C20	C25	121.86
C5	N1	C7	123.27	C12	C13	H13a	109.47
Bi1	N2	C20	124.89	C12	C13	H13b	109.48
Bi1	N2	C18	114.14	C12	C13	H13c	109.47
C20	N2	C18	120.95	H13a	C13	H13b	109.46
Bi1	C4	C3	119.84	H13a	C13	H13c	109.47
Bi1	C4	C16	117.44	H13b	C13	H13c	109.48
C3	C4	C16	122.63	C20	C25	C24	117.23
N1	C5	C3	115.81	C20	C25	C26	121.66
N1	C5	C6	125.39	C24	C25	C26	121.11
C3	C5	C6	118.8	N2	C18	C16	117.25
H27a	C27	H27b	109.47	N2	C18	C19	125.13
H27a	C27	H27c	109.48	C16	C18	C19	117.6
H27a	C27	C21	109.47	H14a	C14	H14b	109.47
H27b	C27	H27c	109.47	H14a	C14	H14c	109.48
H27b	C27	C21	109.47	H14a	C14	C8	109.47
H27c	C27	C21	109.47	H14b	C14	H14c	109.47
H1	C1	C15	119.35	H14b	C14	C8	109.46
H1	C1	C2	119.35	H14c	C14	C8	109.47
C15	C1	C2	121.3	C25	C24	H24	118.52
C27	C21	C20	123.21	C25	C24	C23	122.95
C27	C21	C22	120.68	H24	C24	C23	118.53
C20	C21	C22	116.09	C12	C11	H11	119.2
C4	C3	C5	118.48	C12	C11	C10	121.59
C4	C3	C2	118.76	H11	C11	C10	119.2
C5	C3	C2	122.76	C7	C8	C14	122.67
C1	C15	H15	119.28	C7	C8	C9	119.25
C1	C15	C16	121.44	C14	C8	C9	118.05
H15	C15	C16	119.28	C21	C22	H22	118.34
C1	C2	C3	119.61	C21	C22	C23	123.32
C1	C2	H2	120.18	H22	C22	C23	118.34
C3	C2	H2	120.21	C8	C9	H9	119.5
N1	C7	C12	117	C8	C9	C10	121
N1	C7	C8	121.67	H9	C9	C10	119.5
C12	C7	C8	120.82	C25	C26	H26a	109.47
C7	C12	C13	122.43	C25	C26	H26b	109.47
C7	C12	C11	118.31	C25	C26	H26c	109.48
C13	C12	C11	119.22	H26a	C26	H26b	109.46
C4	C16	C15	116.24	H26a	C26	H26c	109.49
C4	C16	C18	118.22	H26b	C26	H26c	109.47
C15	C16	C18	125.43	C24	C23	C22	118.49
H19a	C19	H19b	109.47	C24	C23	H23	120.76
H19a	C19	H19c	109.48	C22	C23	H23	120.76
H19a	C19	C18	109.46	C11	C10	C9	118.97

Table S4. Contact lengths in the solid-state structure of **$LBiBr_2$**.

Atom1	Atom2	Length [Å]
H19b	Br2	2.905
H22	Br1	2.896
H14b	C10	2.895
C1	C1	3.392
C1	H1	2.863
Br2	H2	2.93
C1	H6a	2.761
C2	H6a	2.875

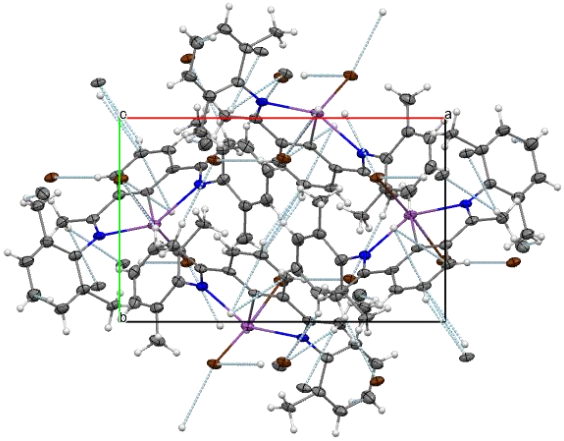


Figure S17. Solid state packing of **$LBiBr_2$** viewed along the *c*-axis.

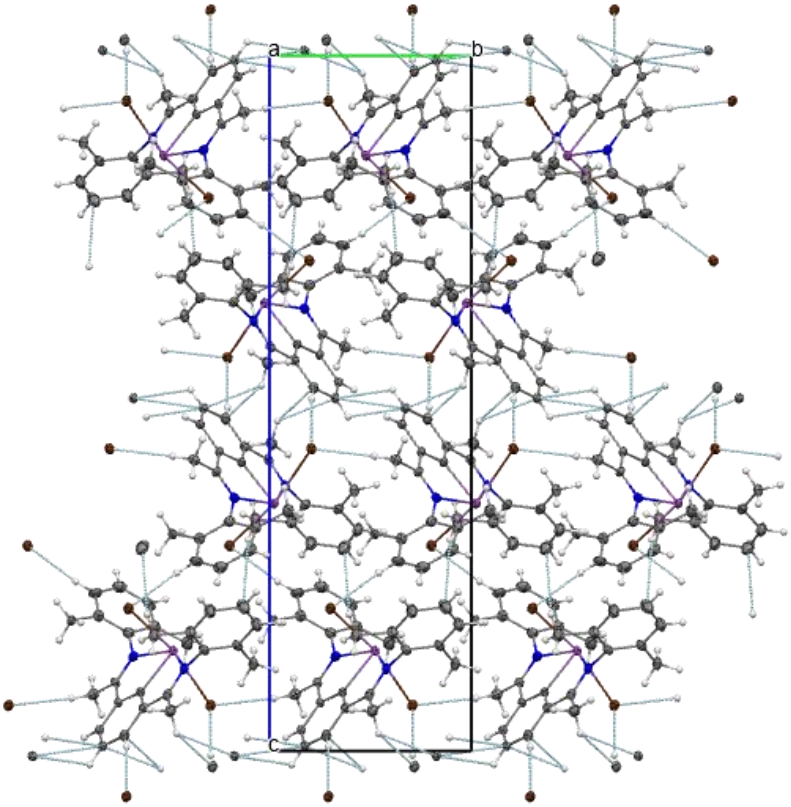


Figure S18. Solid state packing of **$LBiBr_2$** viewed along the *a*-axis.

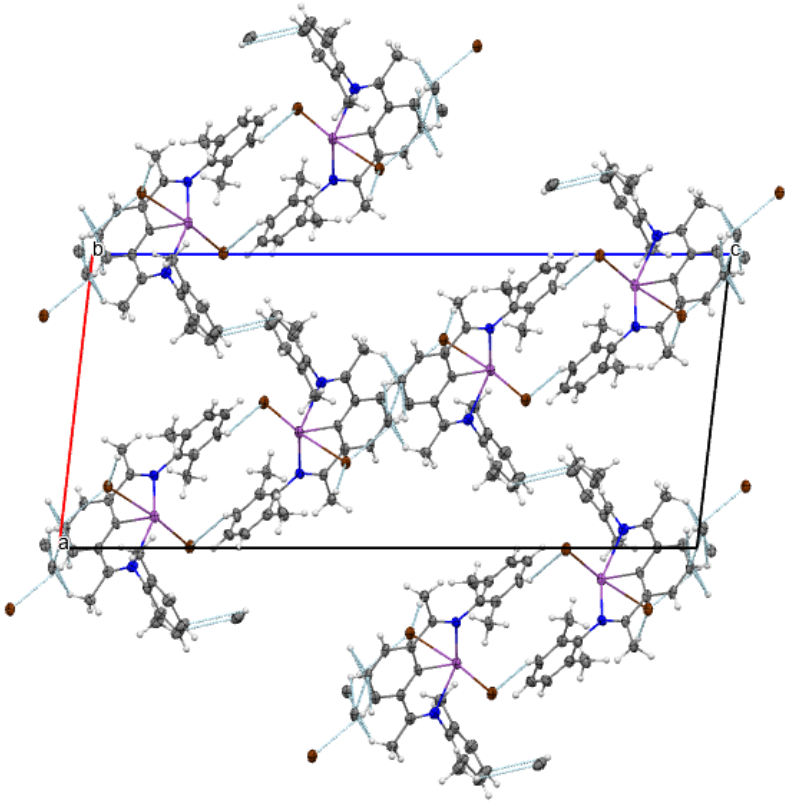


Figure S19. Solid state packing of **LBiBr$_2$** viewed along the *b*-axis.

The bismuth ion itself does not engage in intermolecular interactions, and these are instead restricted to the N,C,N pincer ligand L and the bromide ligands. These include a methyl group from the imine forming an H-arene interaction with the central phenyl ring *d*(C1···H6a) = 2.761(8) Å, as well as halide-H interactions with *d*(Br1···H22) = 2.8959(8) Å, *d*(Br2···H19b) = 2.9048(8) Å and *d*(Br2···H2) = 2.9303(9) Å. The Bi^{3+} center is coordinated in a distorted square pyramidal geometry, (refer to Figure 1c) in which the halides and nitrogen atoms are positioned mutually *trans* to each other, constructing the base of the pyramid, while the carbon atom occupies the apical coordination site. Distortion from the pyramidal coordination is evidenced by the angles of ∠(N1-Bi1-N2) = 142.2(2)° and ∠(Br1-Bi1-Br2) = 168.35(3)°. The xylyl substituents are twisted slightly out of plane, with one methyl group closer to the respective bromide ligand. The Bi-N distances of *d*(Bi-N1) = 2.479(7) Å and *d*(Bi-N2) = 2.454(6) Å are significantly smaller than the sum of the van der Waals radii, confirming coordination and providing the Bi^{3+} ion with 12 valence electrons. Interestingly, there is an asymmetry in the Bi-Br distances, with one measuring *d*(Bi1-Br1) = 2.7576(9) Å as opposed to *d*(Bi1-Br2) = 2.9116(9) Å, and this highlights the exceptional steric shielding of the Bi^{3+} ion in this system.

Table S5. Crystal data and structure refinement for **LBr**.

Identification code	KD102
Empirical formula	$C_{26}H_{27}BrN_2$
Formula weight	447.40
Temperature/K	100
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.5116(9)
b/Å	10.8836(11)
c/Å	24.405(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2260.8(4)
Z	4
ρ_{calc} g/cm^3	1.314
μ/mm^{-1}	1.832
F(000)	928.0
Crystal size/mm^3	0.5 × 0.367 × 0.25
Radiation	Mo K_α (λ = 0.71073)
2Θ range for data collection/°	5.068 to 55.262
Index ranges	-11 ≤ h ≤ 10, -14 ≤ k ≤ 12, -27 ≤ l ≤ 31
Reflections collected	9226
Independent reflections	5108 [R_{int} = 0.0186, R_{sigma} = 0.0222]
Data/restraints/parameters	5108/0/269
Goodness-of-fit on F_2	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0302, wR_2 = 0.0640
Final R indexes [all data]	R_1 = 0.0375, wR_2 = 0.0682
Largest diff. peak/hole / e Å^{-3}	0.43/-0.28
Flack parameter	0.020(6)

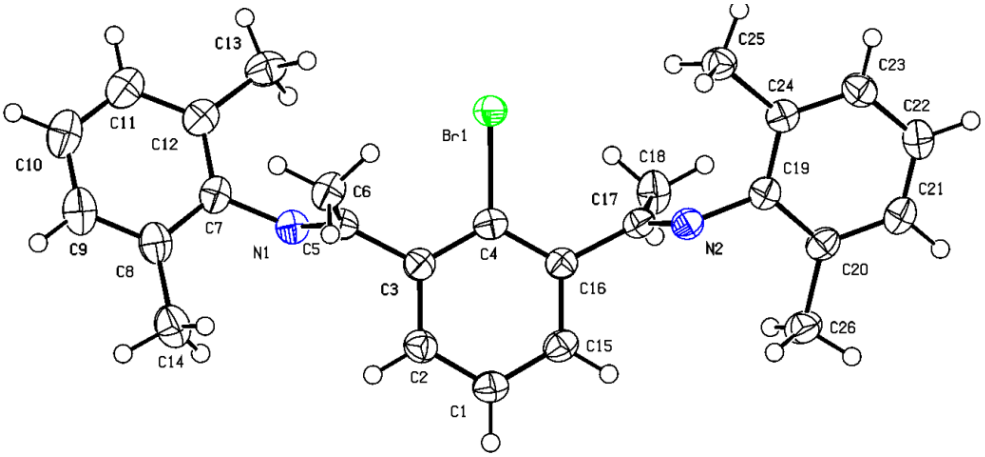


Figure S20. ORTEP plots and atom numbering of **LBr**. Thermal displacement ellipsoids are displayed at the 50% probability level.

Table S6. Bond lengths in the solid-state structure of **LBr**.

Atom1	Atom2	Length [Å]	Atom1	Atom2	Length [Å]	Atom1	Atom2	Length [Å]
Br1	C4	1.924(3)	C2	H2	0.950	C18	H18C	0.980
N2	C19	1.429(5)	C2	C1	1.382(5)	C11	H11	0.950
N2	C17	1.269(5)	C24	C23	1.386(5)	C11	C10	1.387(6)
N1	C5	1.269(4)	C24	C25	1.506(5)	C25	H25A	0.980
N1	C7	1.431(4)	C12	C11	1.393(6)	C25	H25B	0.980
C16	C17	1.504(5)	C12	C13	1.504(6)	C25	H25C	0.980
C16	C4	1.391(5)	C20	C21	1.399(5)	C8	C9	1.401(6)
C16	C15	1.397(5)	C20	C26	1.505(5)	C8	C14	1.501(6)
C19	C24	1.403(5)	C23	H23	0.950	C22	H22	0.950
C19	C20	1.397(5)	C23	C22	1.391(6)	C10	H10	0.949
C17	C18	1.512(5)	C21	H21	0.950	C10	C9	1.389(6)
C3	C4	1.398(5)	C21	C22	1.380(6)	C13	H13A	0.980
C3	C5	1.504(5)	C15	H15	0.950	C13	H13B	0.980
C3	C2	1.393(5)	C15	C1	1.390(5)	C13	H13C	0.980
C5	C6	1.512(5)	C1	H1	0.950	C9	H9	0.950
C7	C12	1.403(5)	C26	H26A	0.980	C14	H14A	0.980
C7	C8	1.398(5)	C26	H26B	0.980	C14	H14B	0.980
C6	H6A	0.980	C26	H26C	0.980	C14	H14C	0.980
C6	H6B	0.980	C18	H18A	0.980			
C6	H6C	0.980	C18	H18B	0.980			

Table S7. Angles in the solid-state structure of **LBr**.

Atom1	Atom2	Atom3	Angle [°]	Atom1	Atom2	Atom3	Angle [°]
C19	N2	C17	119.5(3)	H15	C15	C1	119.7
C5	N1	C7	119.7(3)	C2	C1	C15	120.0(3)
C17	C16	C4	124.1(3)	C2	C1	H1	120.0
C17	C16	C15	117.7(3)	C15	C1	H1	120.0
C4	C16	C15	118.2(3)	C20	C26	H26A	109.4
N2	C19	C24	120.0(3)	C20	C26	H26B	109.5
N2	C19	C20	118.4(3)	C20	C26	H26C	109.4
C24	C19	C20	121.4(3)	H26A	C26	H26B	109.5
N2	C17	C16	117.0(3)	H26A	C26	H26C	109.5
N2	C17	C18	126.7(3)	H26B	C26	H26C	109.5
C16	C17	C18	116.1(3)	C17	C18	H18A	109.5
C4	C3	C5	123.7(3)	C17	C18	H18B	109.4
C4	C3	C2	118.3(3)	C17	C18	H18C	109.5
C5	C3	C2	118.0(3)	H18A	C18	H18B	109.5
Br1	C4	C16	118.8(3)	H18A	C18	H18C	109.5
Br1	C4	C3	119.2(3)	H18B	C18	H18C	109.5
C16	C4	C3	122.0(3)	C12	C11	H11	119.2
N1	C5	C3	117.0(3)	C12	C11	C10	121.5(4)
N1	C5	C6	127.0(3)	H11	C11	C10	119.2
C3	C5	C6	115.7(3)	C24	C25	H25A	109.5
N1	C7	C12	118.7(3)	C24	C25	H25B	109.5
N1	C7	C8	119.2(3)	C24	C25	H25C	109.5
C12	C7	C8	121.9(3)	H25A	C25	H25B	109.5
C5	C6	H6A	109.5	H25A	C25	H25C	109.5
C5	C6	H6B	109.4	H25B	C25	H25C	109.5
C5	C6	H6C	109.5	C7	C8	C9	118.0(3)
H6A	C6	H6B	109.5	C7	C8	C14	120.5(3)
H6A	C6	H6C	109.5	C9	C8	C14	121.4(3)
H6B	C6	H6C	109.5	C23	C22	C21	119.7(4)
C3	C2	H2	119.6	C23	C22	H22	120.2
C3	C2	C1	120.8(3)	C21	C22	H22	120.1
H2	C2	C1	119.6	C11	C10	H10	120.3
C19	C24	C23	118.4(3)	C11	C10	C9	119.4(4)
C19	C24	C25	120.3(3)	H10	C10	C9	120.3
C23	C24	C25	121.3(3)	C12	C13	H13A	109.5
C7	C12	C11	117.9(3)	C12	C13	H13B	109.5
C7	C12	C13	120.4(3)	C12	C13	H13C	109.5
C11	C12	C13	121.6(3)	H13A	C13	H13B	109.4
C19	C20	C21	118.3(3)	H13A	C13	H13C	109.5
C19	C20	C26	120.5(3)	H13B	C13	H13C	109.5
C21	C20	C26	121.2(3)	C8	C9	C10	121.1(4)
C24	C23	H23	119.4	C8	C9	H9	119.5
C24	C23	C22	121.1(3)	C10	C9	H9	119.4
H23	C23	C22	119.4	C8	C14	H14A	109.4
C20	C21	H21	119.5	C8	C14	H14B	109.5

C20	C21	C22	121.1(4)	C8	C14	H14C	109.5
H21	C21	C22	119.4	H14A	C14	H14B	109.5
C16	C15	H15	119.7	H14A	C14	H14C	109.4
C16	C15	C1	120.6(3)	H14B	C14	H14C	109.5

Table S8. Contact lengths in the solid-state structure of **LBr**.

Atom1	**Atom2**	**Length [Å]**
H1	C12	2.895
H18B	C11	2.842

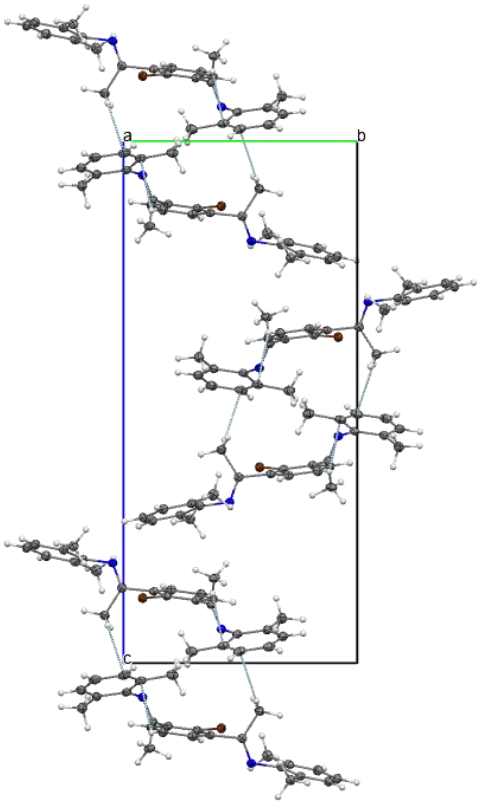


Figure S21. Solid state packing of **LBr** viewed along the *a*-axis.

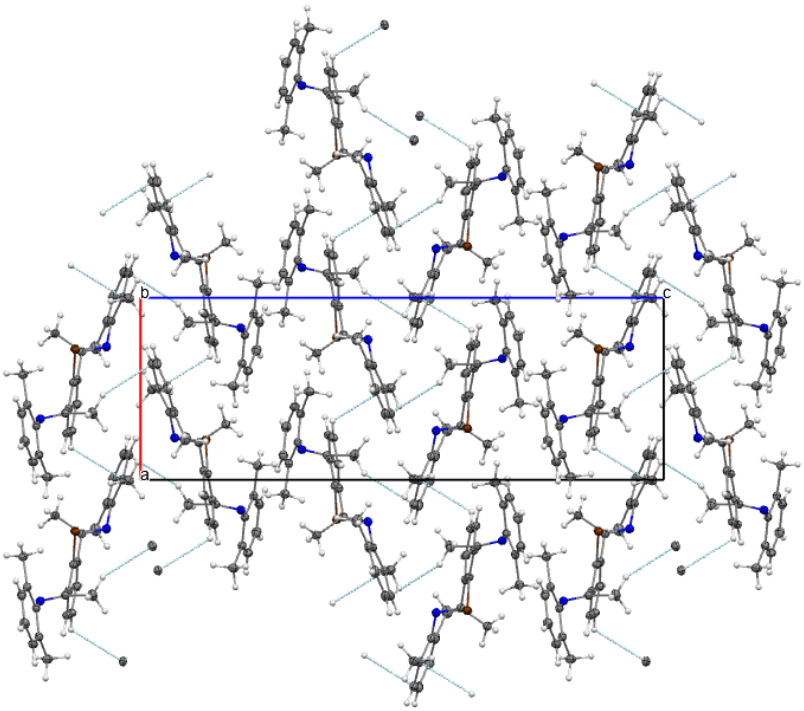


Figure S22. Solid state packing of **LBr** viewed along the *b*-axis.

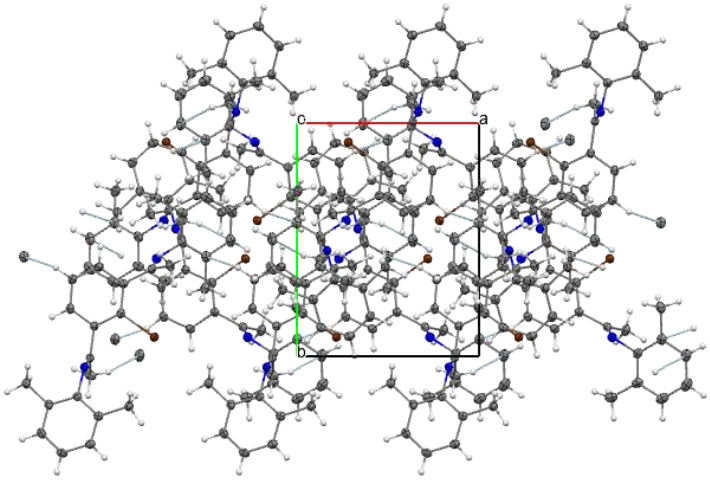


Figure S23. Solid state packing of **LBr** viewed along the *c*-axis.

6. UV-Vis Spectroscopy

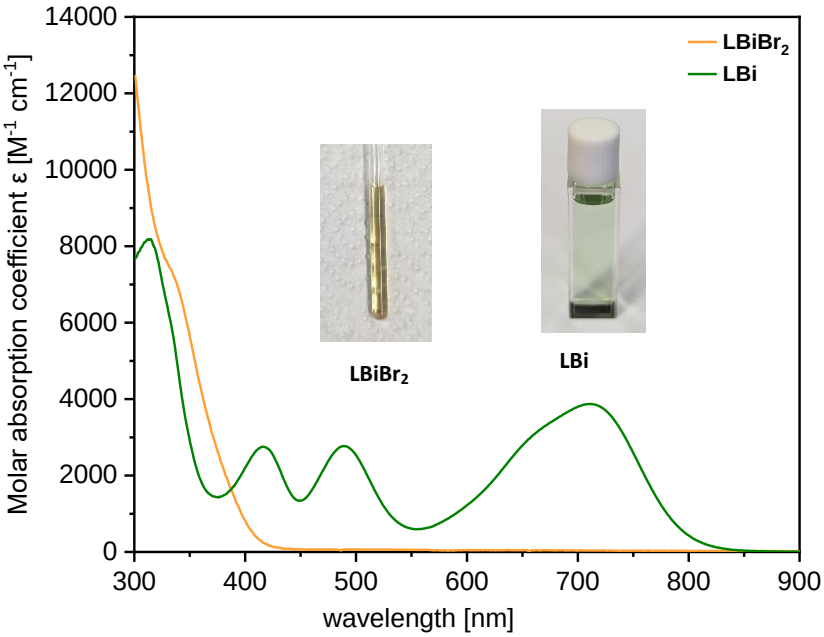


Figure S24. UV-Vis absorption spectra of **LBi** (green) in benzene and **$LBiBr_2$** (orange) in CH_2Cl_2.

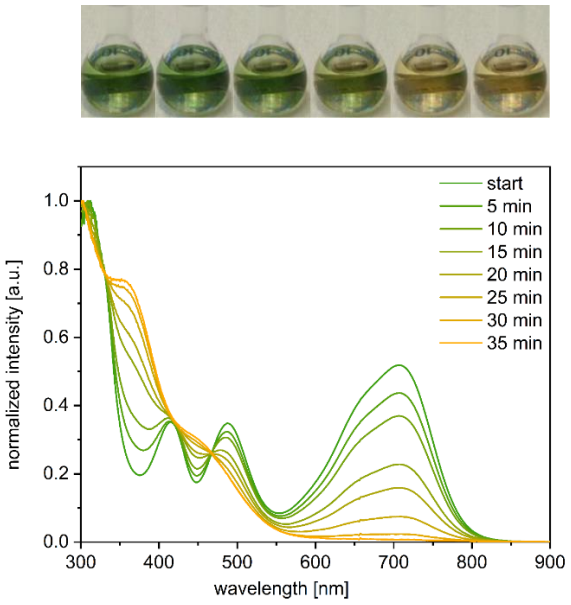


Figure S25. Degradation of **LBi** over the course of 35 minutes as monitored by UV-Vis absorption spectroscopy (bottom), as well as photographs of the corresponding stock solution taken every seven minutes.

7. Photoluminescence Measurements

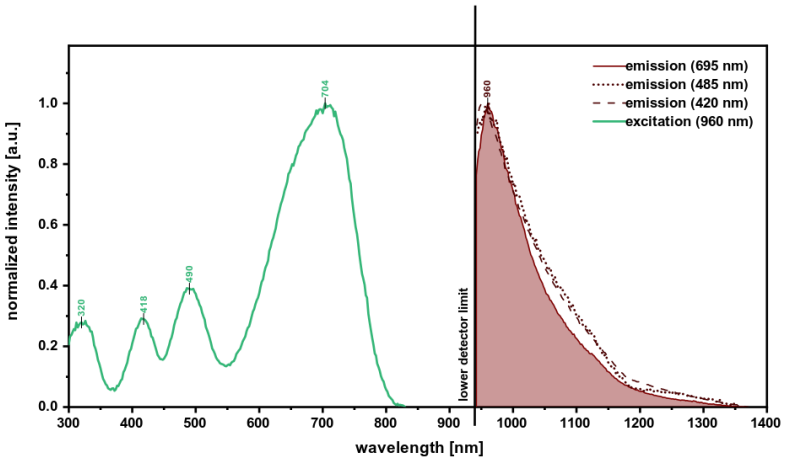


Figure S26. Photoluminescence and excitation spectrum of **LBi** in THF at r.t. under vacuum (left). Monoxponential decay and fitting of the time-resolved emission decay of the phosphorescent NIR emission of **LBi** in THF at r.t. Excitation occurred at differing wavelengths and detection at λ_{det} = 960 nm (right).

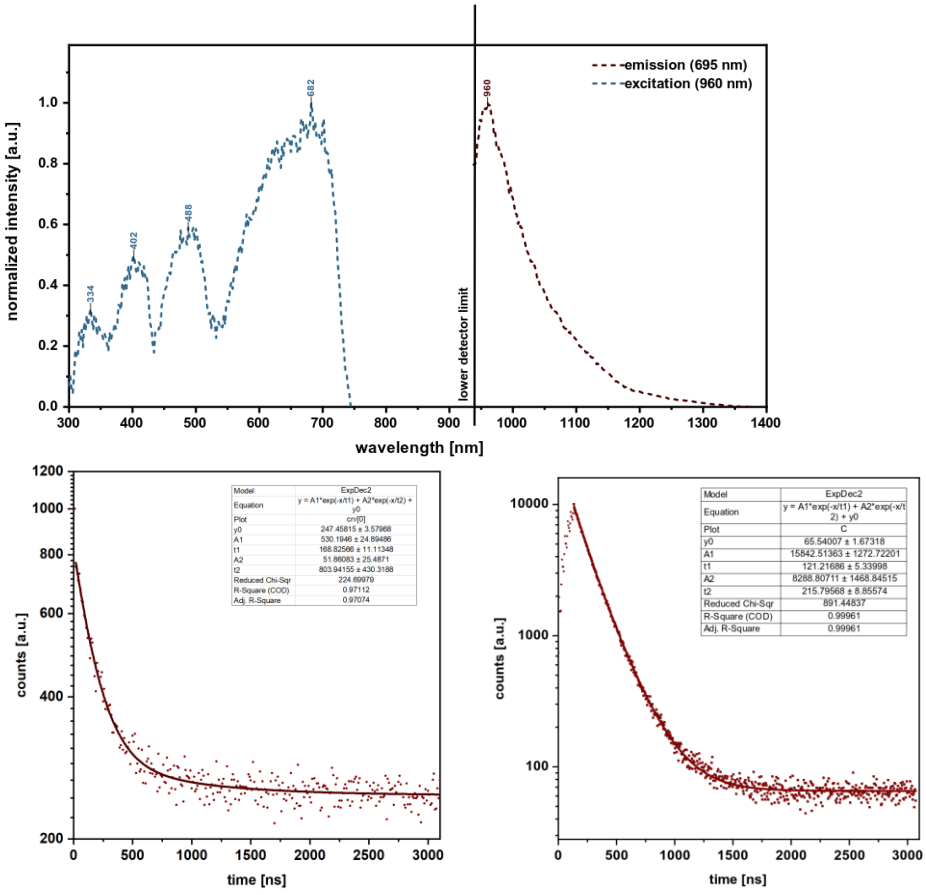


Figure S27. Photoluminescence and excitation spectrum of **LBi** in 2-MeTHF at T = 77 K (left). Biexponential decay and fitting of the time-resolved emission decay of the NIR phosphorescent emission of **LBi** in 2-MeTHF at 77 K. Excitation occurred at λ_{exc} = 420 nm and detection at λ_{det} = 960 nm (right, top). Biexponential decay and fitting of the time-resolved emission decay of the NIR phosphorescent emission of **LBi** in 2-MeTHF at 77 K. Excitation occurred at λ_{exc} = 485 nm and detection at λ_{det} = 960 nm (left, bottom).

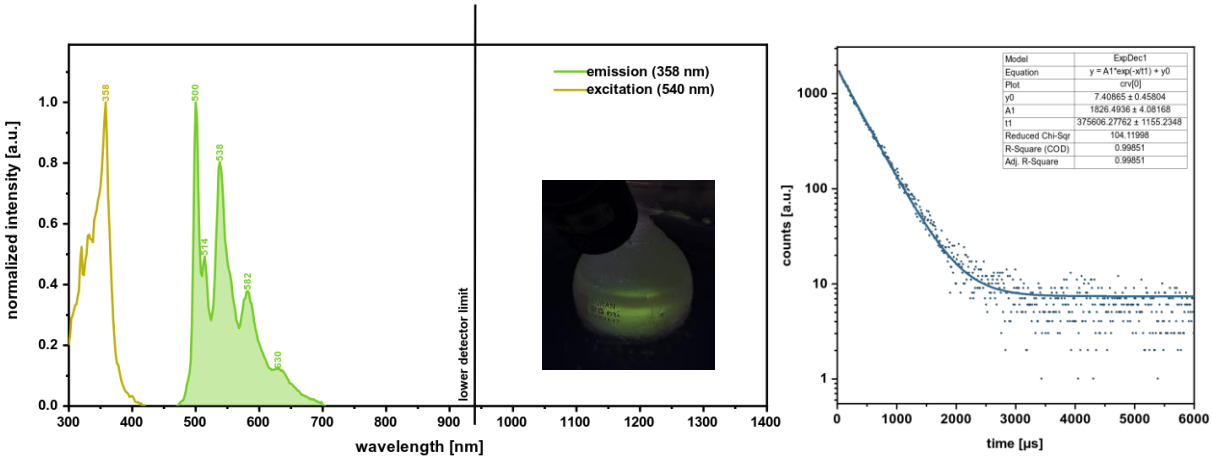


Figure S28. Photoluminescence and excitation spectrum of **LBiBr$_2$** in 2-MeTHF at T = 77 K (left). Monoxponential decay and fitting of the time-resolved emission decay of the phosphorescent emission of **LBiBr$_2$** in 2-MeTHF at 77 K. Excitation occurred at λ_{exc} = 358 nm and detection at λ_{det} = 500 nm (right).

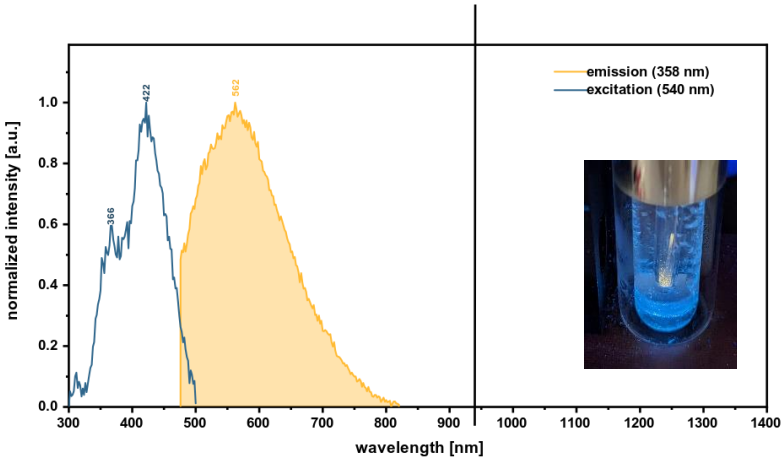


Figure S29. Photoluminescence and excitation spectrum of **LBiBr$_2$** as a powder at T = 77 K. Note: the wide spectrum and resulting necessity for wide detection band gaps (11 nm) is a result of the weak intensity of this emission.

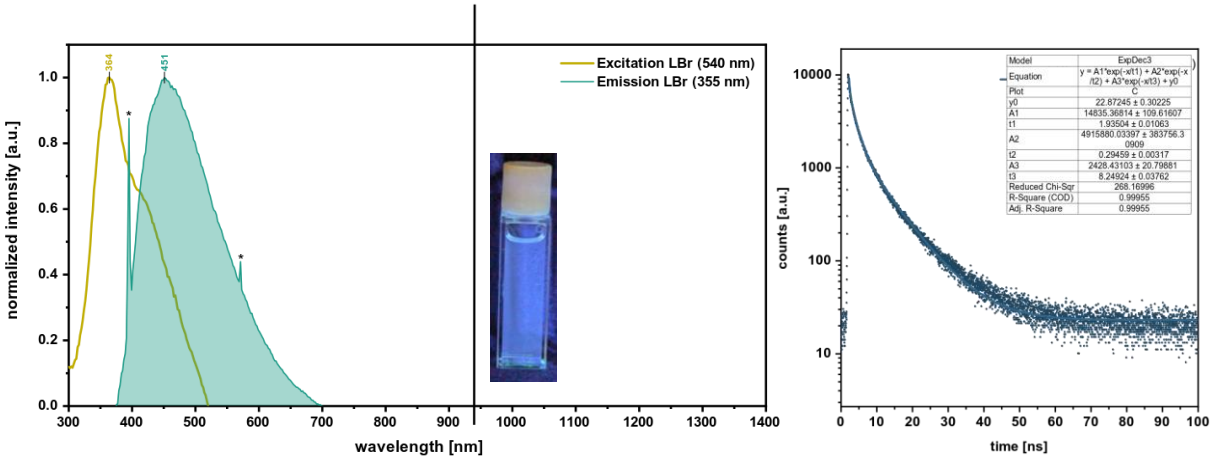


Figure S30. Photoluminescence and excitation spectrum of **LBr** THF at r.t. The QY of this emission is <1%. Note: asterisks mark artefacts that arise from the laser (left). Exponential decay and fitting of the time-resolved emission decay of the emission of **LBr** in THF at r.t. Excitation occurred at λ_{exc} = 355 nm and detection at λ_{det} = 450 nm (right). The QY of this emission is <1%.

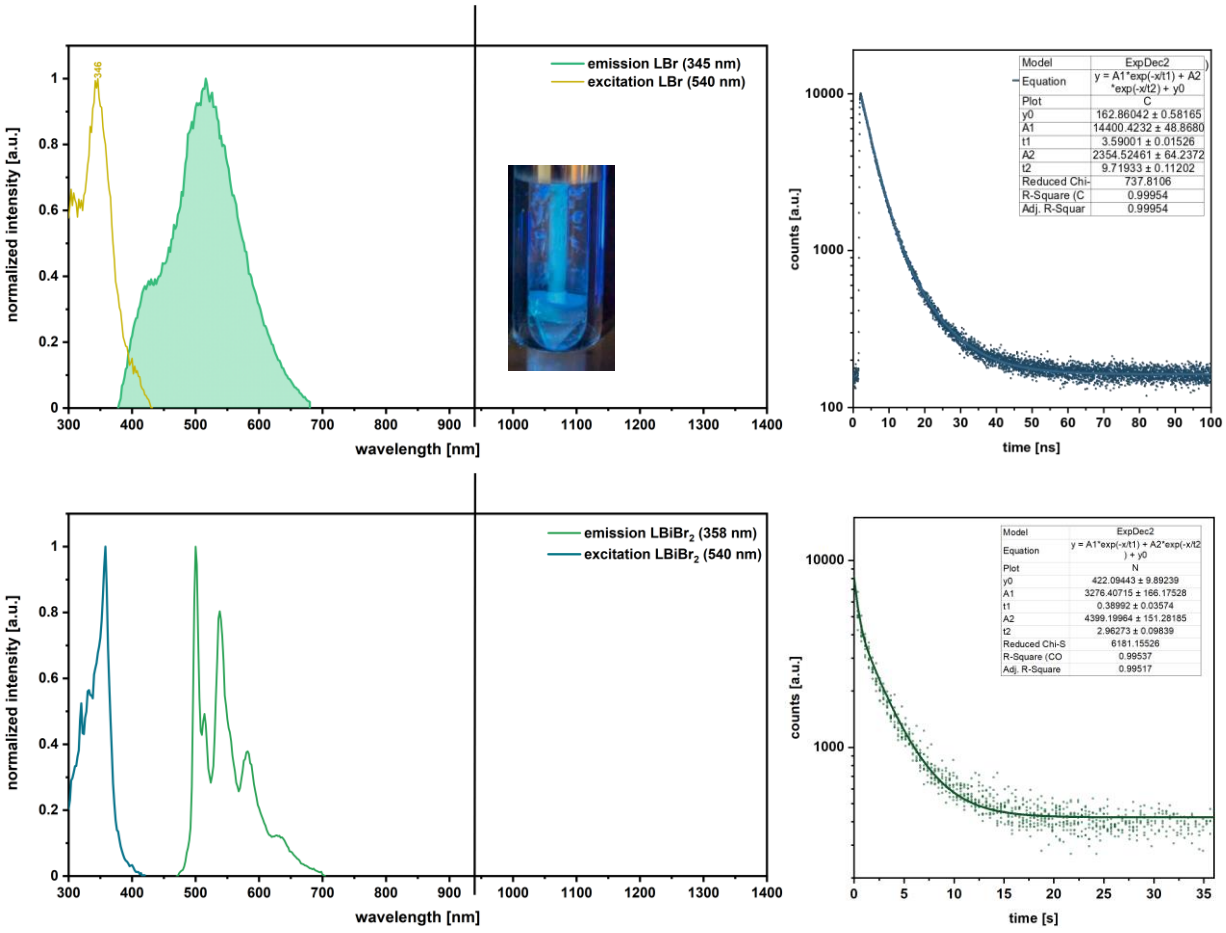


Figure S31. Photoluminescence and excitation spectrum of **LBr** 2-MeTHF at T = 77 K (top left) in comparison with the photoluminescence spectra of **LBiBr$_2$** in 2-MeTHF at T = 77 K (bottom left). Exponential decay and fitting of the time-resolved emission decay of the fluorescence of **LBr** in 2-MeTHF at 77K (top right) and exponential decay and fitting of the time-resolved emission decay of the phosphorescence of **LBr** in 2-MeTHF at 77K (bottom right). Excitation for both emission decay curves occurred at λ_{exc} = 355 nm. The detection of the phosphorescence occurred at λ_{det} = 570 nm, while the detection of the phosphorescence occurred at λ_{det} = 516 nm.

8. TD-DFT Calculations

Table S9. Atomic coordinates of **LBiBr$_2$** for TD-DFT calculations using the Gaussian 16 program package.

C	-0.00005	1.74146	0.68353
C	3.49271	-0.41126	-0.02289
C	-2.46976	1.63274	0.65809
C	-3.49286	-0.41125	-0.02284
N	2.36896	0.44776	0.15225
C	-1.21648	2.36628	0.95136
N	-2.36911	0.44775	0.15233
C	3.77655	2.30210	0.94614
H	3.86139	2.54860	2.01006
H	3.83059	3.24480	0.38983
H	4.61988	1.67406	0.65740
C	-3.93330	-0.71311	-1.32387
C	-0.00004	4.28388	1.78497
H	-0.00004	5.27888	2.21870
C	1.21639	2.36632	0.95127
C	3.67223	-0.68958	2.50667
H	4.09269	-1.42267	3.20121
H	2.58272	-0.71072	2.60862
H	4.02130	0.29864	2.83161
C	1.20948	3.65169	1.51113
H	2.13809	4.16599	1.73866
C	-4.99213	-1.60747	-1.47818
H	-5.34147	-1.82757	-2.48527
C	2.46964	1.63279	0.65792
C	3.93303	-0.71337	-1.32391
C	5.15335	-1.89725	0.88646
H	5.62513	-2.35581	1.75353
C	-1.20956	3.65165	1.51123
H	-2.13817	4.16592	1.73883
C	4.10468	-1.00050	1.10093
C	5.61209	-2.22065	-0.38946
C	3.31031	-0.07147	-2.52846
H	2.27273	-0.39242	-2.67724
H	3.86958	-0.32836	-3.43274
H	3.27740	1.01977	-2.44178
C	-5.15336	-1.89746	0.88639
H	-5.62504	-2.35620	1.75342
C	4.99188	-1.60771	-1.47815
H	5.34113	-1.82800	-2.48523
C	-4.10471	-1.00070	1.10093
C	-5.61219	-2.22065	-0.38955
C	-3.77666	2.30201	0.94648
H	-4.61999	1.67397	0.65776
H	-3.83078	3.24476	0.39025
H	-3.86141	2.54840	2.01043

C	-3.31073	-0.07092	-2.52835
H	-3.87020	-0.32748	-3.43261
H	-2.27322	-0.39198	-2.67742
H	-3.27768	1.02028	-2.44135
C	-3.67217	-0.68997	2.50668
H	-2.58266	-0.71121	2.60858
H	-4.09266	-1.42311	3.20117
H	-4.02114	0.29825	2.83174
Bi	0.00006	-0.18861	-0.36768
Br	0.00015	1.54695	-2.64195
Br	0.00011	-1.56113	2.07421
C	-6.72256	-3.21441	-0.58777
H	-6.32364	-4.22832	-0.72035
H	-7.39569	-3.23998	0.27507
H	-7.31477	-2.98013	-1.47832
C	6.72247	-3.21440	-0.58761
H	7.39543	-3.24012	0.27536
H	6.32354	-4.22829	-0.72041
H	7.31486	-2.98002	-1.47802

Table S10. Atomic coordinates of the singlet ground state of **LBiBr$_2$** for SOC-corrected calculations using ORCA.

C	4.29735665243139	3.79606574074262	0.46224345907562
C	5.94079896008075	1.86355808087569	3.72599419775269
C	2.68814628894838	3.57237779576208	-1.37859691309074
C	1.58299506123917	1.48261415233135	-1.59513490386568
N	5.38716440416923	2.64756987910515	2.68396727974378
C	3.72028092077158	4.34993730748172	-0.66823345996793
N	2.37250409504963	2.42455017135415	-0.89468100025173
C	6.96258385186798	4.47034022903835	3.09405101999259
H	6.60811129971615	5.44718117105638	3.43349481262564
H	7.81711495670008	4.64843299399008	2.43682001840798
H	7.28469574763937	3.88859856231178	3.95424527297643
C	2.08645559748251	0.89364180942996	-2.76468082061993
C	5.16994494109832	6.25583241538329	-0.42441609803713
H	5.51414844492531	7.22166895272875	-0.77370891810443
C	5.30083840223171	4.44760490996237	1.15878503362161
C	3.98215820380638	2.51483612776909	5.16863478997475
H	3.63428190895390	2.36964253171470	6.19152568333352
H	3.18069778962432	2.20238349987271	4.49357346677820
H	4.12368569717589	3.58507423101311	4.99894772470427
C	5.74381672245928	5.68972959590676	0.70347056134846
H	6.53327093775444	6.22079397445032	1.22131410988945
C	1.32885026538662	-0.10229982004952	-3.37379951292517
H	1.71593612319034	-0.57216241569184	-4.27177531880272
C	5.87242266477675	3.78723762075417	2.34833150790685
C	7.14090814914208	1.17642544722597	3.50362193588532
C	5.76701049875927	0.92528653959899	5.92174354526075
H	5.23742732883625	0.84000393931797	6.86468356491290

C	4.16343404691645	5.59578238348753	-1.11278648264870
H	3.73452311390270	6.05543260390761	-1.99482613271177
C	5.24273095086835	1.74848284599995	4.93225734715632
C	6.94386444706861	0.22427392263991	5.71788460154162
H	7.33530659076504	-0.42060672880293	6.49653700968099
C	7.91187542469065	1.32370935484405	2.22962874982095
H	7.26199648512190	1.26293771086345	1.35516318138638
H	8.66757787029846	0.54128048267121	2.15446067273960
H	8.43164229882724	2.28575029313277	2.18772267198940
C	-0.37365977449806	0.10177354546426	-1.70510318719173
H	-1.33297725631612	-0.19602701469832	-1.29559136402326
C	7.62121313165022	0.35437181201509	4.51774276173033
H	8.54608389688743	-0.18852917869583	4.35393028340166
C	0.35391547173205	1.08776222418675	-1.05189859493882
C	0.10890795264067	-0.49788293694267	-2.85663862318855
H	-0.46560709137155	-1.27444921805409	-3.34860114806389
C	2.06840511184523	4.15051562255025	-2.59892216877322
H	1.30046114783838	3.49746784661749	-3.00591731876345
H	2.82612478522992	4.34099741627863	-3.36235440580745
H	1.62249295207658	5.11522782435271	-2.34245508740298
C	3.39142953011553	1.29380711214685	-3.37973397736992
H	3.80298396576636	0.46221966921238	-3.95283706992319
H	4.12656906859694	1.58548437919426	-2.63004611581510
H	3.26226253102190	2.13176629296858	-4.07136921437610
C	-0.18089754667806	1.71762265490151	0.19244536362924
H	0.38072662562600	1.40383326198999	1.07814961880967
H	-1.22039288784695	1.42805548789557	0.34845374570981
H	-0.11936900556655	2.80639744912524	0.16058965650403
Bi	3.43337329429359	1.94867208354011	1.28261135039577
Br	5.15052066001351	0.35562672584584	-0.22926715022860
Br	1.67087629426569	3.89821862792523	2.49064998820544

Table S11. Atomic coordinates of the triplet state of **LBiBr$_2$** for SOC-corrected calculations using ORCA.

C	4.32128440684313	3.89612443008312	0.44207054763243
C	6.00355304969605	1.89323143058271	3.61935643195738
C	2.73619836499248	3.62429431807628	-1.40941544349758
C	1.74057966915373	1.47688716550088	-1.66108633329900
N	5.50371618140873	2.67794151240543	2.55547425666876
C	3.66346172186846	4.45681933781085	-0.64981166313104
N	2.59831481325948	2.39912590073196	-1.01830378311604
C	6.86215882208192	4.61236025903386	3.19519670662064
H	6.39671328644393	5.46279141404686	3.70062151462889
H	7.66645746901905	5.00593464703654	2.56946239547834
H	7.28662674098024	3.94707044293282	3.94411274845493
C	2.24924600436451	0.69190533090983	-2.69985643887079
C	4.82950357591293	6.51543933798169	-0.17419848716074
H	5.02922659589840	7.55192161151862	-0.41665958650627

C	5.22750102698890	4.59673307653854	1.23416437384967
C	4.29261275708528	2.96293392401942	5.12628877929052
H	3.84473473571138	2.79223688081032	6.10548679724912
H	3.50731113898491	2.89240966773757	4.37068228591777
H	4.67297035256441	3.98883835521487	5.10559660978356
C	5.47668958477337	5.92879526402969	0.90637413284502
H	6.17307316894053	6.51561848489030	1.49402166130378
C	1.41631774596153	-0.26991910758802	-3.26005986727143
H	1.79872262143184	-0.89022477175612	-4.06367603393866
C	5.85824985085302	3.90491007283443	2.35435475028459
C	7.06028128117024	1.01277426690184	3.36989211205967
C	5.83417701106819	1.12496192283040	5.87597999373276
H	5.36027371070703	1.17115042872323	6.85077748074999
C	3.93169224589080	5.79218892114239	-0.94927876852511
H	3.44178022361501	6.27370372317117	-1.78766442552185
C	5.38573583237970	1.97447860184546	4.87104570844995
C	6.86798376083569	0.23144484393748	5.64707787212208
H	7.20130429751629	-0.42762754085961	6.44075166149100
C	7.73909325597674	0.98776095746172	2.03714392331963
H	7.03705862118842	0.75815780768908	1.23124807978995
H	8.52664339222686	0.23410748537795	2.02422731030395
H	8.18933072086375	1.95689195690181	1.80364337990955
C	-0.37081129338505	0.36493465358727	-1.79092756691108
H	-1.39171302698166	0.24441585534042	-1.44439613707513
C	7.47939656269212	0.18469446121802	4.40449909480260
H	8.29852124614934	-0.50366373490028	4.22560557369192
C	0.42817898891950	1.33676137595299	-1.20008064038668
C	0.11783769809375	-0.43958249785382	-2.80767819136201
H	-0.51713093022806	-1.19753591049883	-3.25237445692385
C	2.00129016156197	4.19888374537786	-2.56949897165228
H	1.34573465221502	3.46076538756212	-3.02665988469050
H	2.70854807421797	4.55951544906260	-3.32050449811977
H	1.40344033925676	5.05537497509579	-2.24818387610856
C	3.63858299902751	0.90300787697848	-3.21213082776335
H	3.90077428427775	0.12961914580501	-3.93428777561136
H	4.37102945997635	0.88035598744922	-2.40218914646061
H	3.73460784997782	1.87408681480456	-3.70767377573327
C	-0.10765925734228	2.22628000753213	-0.12354404255725
H	0.47566760246417	2.13895627079244	0.79677839958524
H	-1.14183544408447	1.96762272192161	0.10477292929115
H	-0.07851489197303	3.27761436625612	-0.42391565118934
Bi	3.89194287028155	1.83107254761991	0.95109749301373
Br	4.70880999100187	-0.79471720050405	0.09991509891058
Br	2.03272402522373	0.76426534089475	2.87663617019439

Table S12. Atomic coordinates of **LBi** for TD-DFT calculations using Gaussian 16 program package.

C	0.00007	1.83840	-0.00006
C	-3.41827	-0.41673	-0.00000

C	2.45390	1.76856	-0.00003
C	3.41876	-0.41689	0.00002
N	-2.31491	0.47272	-0.00007
C	1.22436	2.54820	-0.00005
N	2.31502	0.47216	-0.00005
C	-3.79112	2.45165	-0.00001
H	-3.89885	3.09308	-0.88237
H	-3.89883	3.09303	0.88240
H	-4.60491	1.72375	-0.00003
C	3.92876	-0.88640	1.22258
C	0.00043	4.64244	-0.00003
H	0.00059	5.72838	-0.00002
C	-1.22405	2.54854	-0.00006
C	-3.38995	-0.36939	-2.52652
H	-3.81483	-0.92227	-3.36948
H	-2.29769	-0.45790	-2.56675
H	-3.62468	0.69307	-2.67078
C	-1.20797	3.94805	-0.00004
H	-2.13983	4.50834	-0.00003
C	4.95878	-1.82703	1.19580
H	5.35329	-2.19428	2.14187
C	-2.45368	1.76919	-0.00005
C	-3.93172	-0.88238	1.22258
C	-4.96629	-1.81814	-1.19561
H	-5.36824	-2.17749	-2.14160
C	1.20866	3.94768	-0.00003
H	2.14066	4.50773	-0.00002
C	-3.93165	-0.88262	-1.22253
C	-5.49595	-2.30400	0.00013
C	-3.39007	-0.36891	2.52650
H	-2.29780	-0.45731	2.56676
H	-3.81491	-0.92170	3.36954
H	-3.62490	0.69356	2.67060
C	4.95880	-1.82716	-1.19557
H	5.35334	-2.19452	-2.14160
C	-4.96635	-1.81791	1.19579
H	-5.36833	-2.17708	2.14182
C	3.92880	-0.88655	-1.22249
C	5.49071	-2.31065	0.00015
C	3.79138	2.45096	0.00004
H	4.60507	1.72296	-0.00004
H	3.89914	3.09227	0.88249
H	3.89913	3.09247	-0.88227
C	3.38234	-0.37843	2.52663
H	3.80442	-0.93448	3.36892
H	2.28991	-0.46672	2.56294
H	3.61685	0.68341	2.67561
C	3.38240	-0.37872	-2.52661

H	2.28998	-0.46704	-2.56294
H	3.80453	-0.93483	-3.36883
H	3.61688	0.68312	-2.67567
Bi	-0.00056	-0.30167	-0.00007
C	-6.58523	-3.34114	0.00020
H	-7.22215	-3.25313	0.88658
H	-7.22226	-3.25314	-0.88611
H	-6.16651	-4.35594	0.00017
C	6.61910	-3.30519	0.00018
H	6.58555	-3.94860	-0.88516
H	7.59411	-2.80042	-0.00142
H	6.58732	-3.94653	0.88708

Table S13. Atomic coordinates of the triplet state of **LBi** for SOC-corrected calculations using ORCA.

Bi	18.27567475681291	2.36946785281932	0.98367618879633
C	16.05919722147381	2.65947489081853	-1.58793201792648
N	19.91795314554489	1.48796979080513	2.54690819655962
N	16.96828030117461	1.76742026164213	-0.98513031518235
C	19.65333115546782	-0.39795023459216	1.19893253508516
C	18.72864263280894	0.34420841302872	0.44099671009409
C	15.62633943547339	4.48357597026000	-3.07776830141595
H	15.97590489022268	5.18803390045968	-3.82546899047816
C	20.27748162710051	0.26268120962184	2.33096015631330
C	20.44519604125951	2.26097997705809	3.60062474818253
C	19.93475178137557	-1.71542800141948	0.84237550299562
H	20.64371741122311	-2.29883640940142	1.41934891122860
C	19.78066108724817	2.28504214191579	4.83131951316456
C	14.72826986160651	2.67020821136302	-1.15686526271123
C	18.10003376248480	-0.24842583245122	-0.66973640948658
C	16.52396445154799	3.56205175642160	-2.55036972273798
C	18.40014197295179	-1.56682023833677	-1.00687794370788
H	17.92361657339657	-2.03532423895694	-1.86095540163787
C	21.58137267524110	3.04316466069175	3.36700312966711
C	14.30469694096164	4.51145605387249	-2.66250255527590
H	13.61829589241145	5.23869280906671	-3.08148195957560
C	19.31031395801277	-2.29655729327286	-0.25329887237376
H	19.53551769756896	-3.32150924497454	-0.52251977722003
C	13.86298751622203	3.60747744302495	-1.70975039067428
H	12.82846492827240	3.62350515813977	-1.38260821496909
C	17.15244041124256	0.56034388326098	-1.41574295245306
C	16.44770378985418	0.00075357160935	-2.60652454583875
H	15.78781404560067	0.73924356376467	-3.05819076057863
H	15.85468654146853	-0.87303762014256	-2.32470278540488
H	17.17155942832931	-0.32761171338606	-3.35641217841675
C	20.27758317897255	3.11181761293506	5.83277759181441
H	19.76989877181780	3.13707425567063	6.79150794299289
C	21.40104307905744	3.89482473644240	5.62050759329489
H	21.77322739053255	4.53714300747195	6.41072473169176

C	21.27280649450454	-0.45824107572408	3.17749027780788
H	21.66828273233834	0.18808814929788	3.95892849145425
H	22.10361109816570	-0.82040020369813	2.56716321923936
H	20.81127812761627	-1.33108428354793	3.64693073069009
C	14.25016984150377	1.68446401203279	-0.13823197503781
H	14.24973619205525	0.66602400301371	-0.53901912548382
H	13.23440194636775	1.92122061264845	0.17959734241269
H	14.90177326588439	1.67630407639407	0.74006159573285
C	22.04565852029687	3.85647053214165	4.39443455703383
H	22.92618693797941	4.46702966478960	4.22319589641149
C	22.28327431384090	2.98881963220544	2.04699683754706
H	22.73582717434304	2.00704199555063	1.87726914629436
H	23.07394366795300	3.73815733694491	1.99987126564920
H	21.58626803906200	3.15958809566985	1.22164253495588
C	17.94618987311018	3.51614273055102	-3.01185767850279
H	18.63827477621048	3.54535276011607	-2.16568442669993
H	18.16397096594401	4.35468504819694	-3.67388036665525
H	18.15598739584699	2.58999021043951	-3.55589046243500
C	18.57597792335613	1.42902702742589	5.06384303434013
H	18.83582654336041	0.36595216550588	5.05582049653395
H	17.82936876507674	1.57481347756005	4.27815810976590
H	18.12128305044292	1.65812472725507	6.02796140512998

Table S14. Atomic coordinates of the triplet state of **LBi** for SOC-corrected calculations using ORCA.

Bi	18.29346596547557	2.32586893948558	0.95717138499609
C	16.08406560091066	2.67255356865839	-1.57854400136832
N	19.91055478899443	1.51098589258910	2.52567739473235
N	17.00387511114963	1.79242342924900	-0.98737231035334
C	19.64062857860193	-0.44180410485838	1.21814201363315
C	18.72854234622992	0.26114228648468	0.43469183137780
C	15.63445118891509	4.54435752031017	-3.01400391464216
H	15.98554784718499	5.29159707339331	-3.71838656682865
C	20.24837169717733	0.25368367091939	2.31778965421045
C	20.44755227001444	2.28324961777869	3.56857547723508
C	19.91246780710833	-1.80089576142460	0.87508477151889
H	20.60956415022934	-2.39234296277797	1.45516725303049
C	19.79832625365125	2.31815918129668	4.80896406455286
C	14.73382506906511	2.62038491126882	-1.20720903561044
C	18.07724276928843	-0.29231584523125	-0.66684627023285
C	16.54502993521894	3.63802422773167	-2.48262477785727
C	18.36293235574836	-1.65170176602956	-0.99822649850410
H	17.88337642655664	-2.13021249322492	-1.84290545338611
C	21.58796838407795	3.06024147936752	3.32927213619754
C	14.29541863534678	4.50056784250684	-2.65960883648610
H	13.59694570423674	5.21444626248089	-3.08173235798306
C	19.26573384406067	-2.36072314411730	-0.21800436819169
H	19.47577600802884	-3.39480954646556	-0.47426264171541
C	13.85313736947344	3.54290283411174	-1.76076860941953

H	12.80630307504148	3.50646346531623	-1.47670477979252
C	17.16506291622002	0.54491075870817	-1.39095137302705
C	16.44677133657942	-0.00797106465040	-2.57417580272710
H	15.81756241933457	0.74107975684277	-3.05190690787967
H	15.82174894961200	-0.85769485553672	-2.28161835138899
H	17.16498164494184	-0.38584375194084	-3.30817817867545
C	20.31304603146572	3.13687845387361	5.80808732712539
H	19.81606512600630	3.16539455168509	6.77247287273056
C	21.44279114164098	3.90856341213538	5.58609890905307
H	21.83105111855039	4.54384348253976	6.37434731643993
C	21.23165427183058	-0.46065408129524	3.18004504133320
H	21.64484565094275	0.19058874379383	3.94830533858538
H	22.05130209262300	-0.85688297935579	2.57329181618142
H	20.75681519383951	-1.31941167680888	3.66541506654980
C	14.25533423328446	1.59088913589504	-0.23294310969897
H	14.34472946048262	0.57915599929469	-0.63907666175486
H	13.20913532043416	1.76029662588818	0.02368996058655
H	14.84732388509501	1.61092400977891	0.68663017665118
C	22.07255662853280	3.86751052063626	4.35221327845208
H	22.95709262044125	4.47020168196026	4.17301405375200
C	22.27241857769433	3.00570245357738	1.99999228587948
H	22.66925682529440	2.00684550115437	1.79628438584450
H	23.09968203030668	3.71517160584431	1.96142035265034
H	21.57948782775675	3.23637787031540	1.18557317647112
C	17.98808712683053	3.67609700899401	-2.87612062435349
H	18.63512427249027	3.84094641641019	-2.00910834217672
H	18.17097476251133	4.47543074753075	-3.59510332769660
H	18.30373624059185	2.72970013056355	-3.32363551716938
C	18.58065986854126	1.48246814336043	5.04893575429210
H	18.80225578365595	0.41554633934431	4.95483939629426
H	17.79662174326548	1.70351446328204	4.31853073299402
H	18.18158371741578	1.66085501735990	6.04792039556864

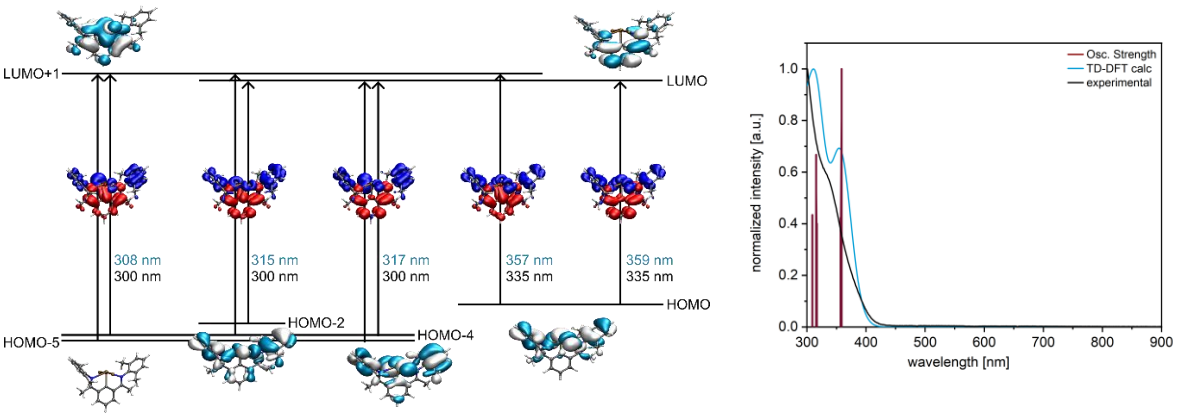


Figure S32. Left: Relevant pbe1pbe/6-31G(d)PCM (CH_2Cl_2)-calculated electronic transitions of **LBiBr$_2$** with the calculated wavelengths in light blue. Contour plots of respective acceptor and donor molecular orbitals are shown in light blue and white colours and the corresponding electron density difference maps (EDDMs) in red and blue with electron density gain in red and electron density loss in blue. The values in black represent the wavelengths of the experimentally detected electronic transitions; **Right:** Comparison of the experimental and TD-DFT computed absorption spectra of **LBiBr$_2$**.

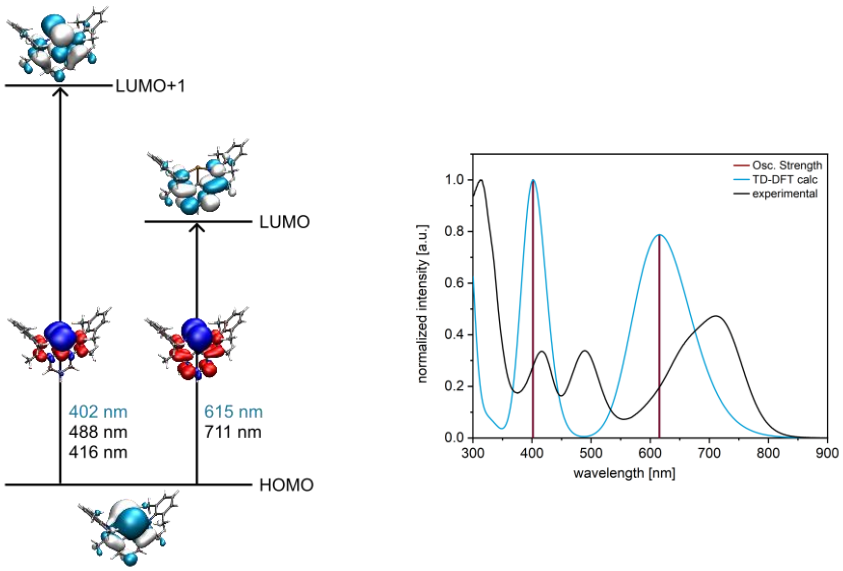


Figure S33. Left: Relevant pbe1pbe/6-31G(d)PCM (benzene)-calculated electronic transitions of **LBi** with the respective wavelengths in light blue. The respective acceptor and donor molecular orbitals are shown in light blue and white colours and the corresponding electron density difference maps (EDDMs) in red and blue with electron density gain in red and electron density loss in blue. The values in black represent the wavelengths of the experimentally detected electronic transitions; **Right:** Comparison of the experimental and TD-DFT computed absorption spectra of **LBi**.

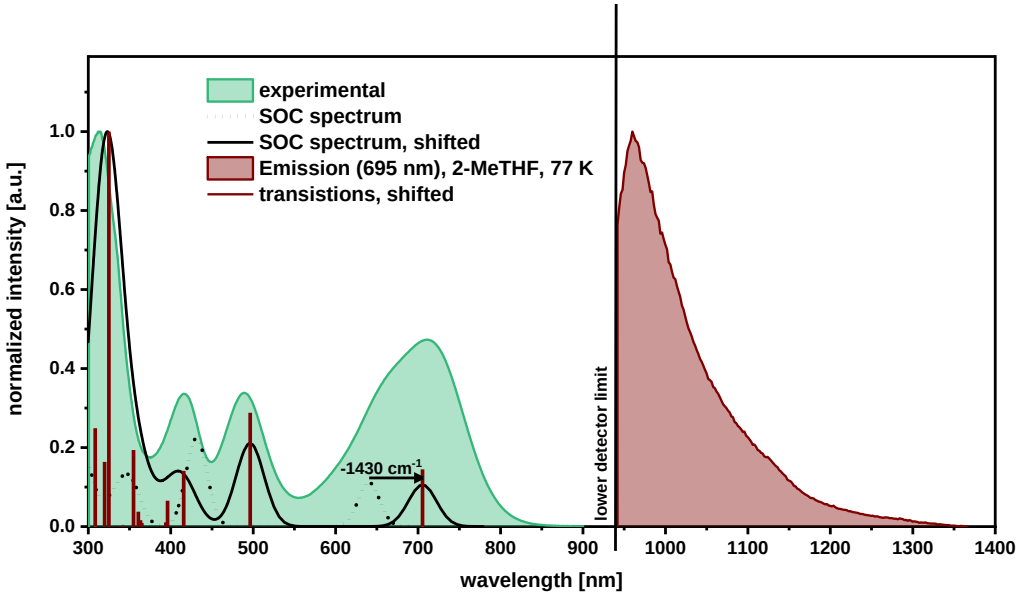


Figure S34. Comparison of experimental and calculated spectra. Calculations were done using the PBE0-function (PBE0) with the SARC-ZORA-TZVP basis set for Bi and the ZORA-def2-TZVP basis and the SARC/J decontracted def2/J auxiliary basis for all other elements.

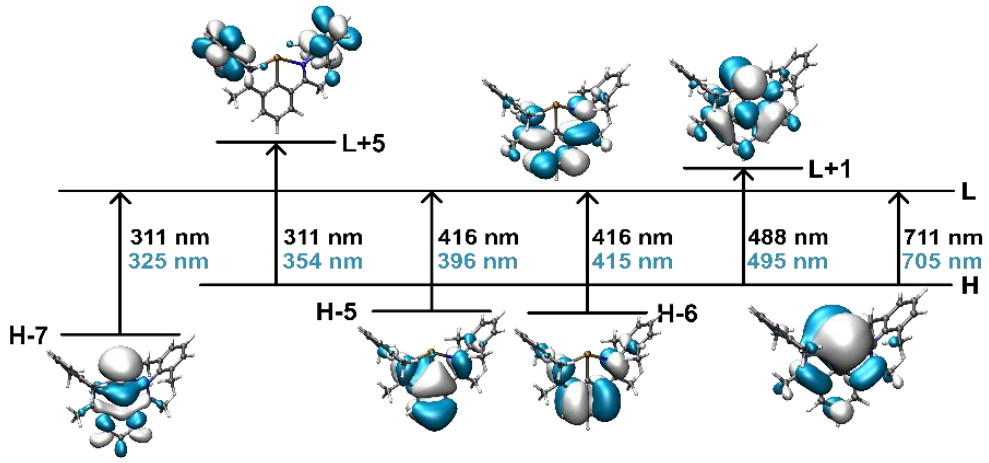


Figure S35. MO Scheme of all relevant calculated electronic transitions with osc. strength greater 5% (normalized) of **LBi** using ORCA with the respective wavelengths in light blue. The values in black represent the wavelengths of the experimentally detected electronic transitions. Contour diagrams of the respective acceptor and donor molecular orbitals are shown in light blue and white colours. Calculations were done using the PBE0-function (PBE0) with the SARC-ZORA-TZVP basis set for Bi and the ZORA-def2-TZVP basis and the SARC/J decontracted def2/J auxiliary basis for all other elements.

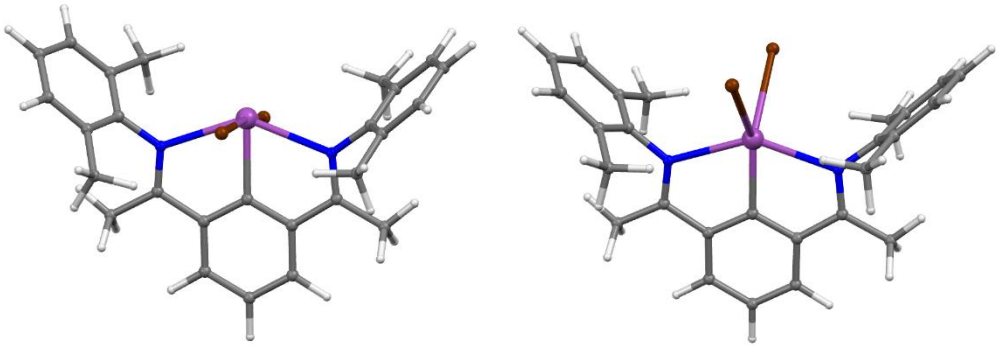


Figure S36. Depictions of the optimized calculated structure of **$LBiBr_2$** for the singlet (left) and triplet excited states $S_1$and T_1 (right). Calculations were done using the PBE0-function (PBE0) with the SARC-ZORA-TZVP basis set for Bi and the ZORA-def2-TZVP basis and the SARC/J decontracted def2/J auxiliary basis for all other elements using ORCA.

Table S15. Calculated eigenvectors of the SOC matrix. Note that the correction factor of 1430 cm^{-1} has not been subtracted from these values.

	E(cm-1)	Weight	Real	Imag	: Root	Spin	M_s
STATE 0:	0.00						
		0.93871	0.96887	-0.00000	: 0	0	0
		0.02518	0.15474	0.03514	: 3	1	-1
		0.02518	0.15474	-0.03514	: 3	1	1
STATE 1:	13913.17						
		0.01857	-0.00000	-0.13627	: 16	0	0
		0.56996	0.75496	-0.00000	: 1	1	0
		0.20415	0.44879	-0.05236	: 1	1	-1
		0.20415	-0.44879	-0.05236	: 1	1	1
STATE 2:	13920.97						
		0.32801	0.57272	0.00000	: 1	1	0
		0.32499	-0.51117	-0.25239	: 1	1	-1
		0.32499	0.51117	-0.25239	: 1	1	1
STATE 3:	13921.51						
		0.08020	0.06861	-0.27476	: 1	1	0
		0.44900	0.59141	0.31501	: 1	1	-1
		0.44900	0.67008	-0.00000	: 1	1	1
STATE 4:	16568.42						
		0.96969	0.98473	0.00000	: 1	0	0
		0.01532	0.00000	-0.12378	: 18	1	0
STATE 5:	17387.43						
		0.53170	0.72918	0.00000	: 2	1	0
		0.02874	0.16952	0.00000	: 3	1	0
		0.18998	0.43411	-0.03906	: 2	1	-1
		0.02621	-0.14811	-0.06535	: 3	1	-1
		0.18998	-0.43411	-0.03906	: 2	1	1
		0.02621	0.14811	-0.06535	: 3	1	1
STATE 6:	17402.12						
		0.32160	0.56710	-0.00000	: 2	1	0
		0.04918	-0.22177	-0.00000	: 3	1	0
		0.29331	-0.49582	-0.21789	: 2	1	-1
		0.01760	-0.13211	0.01207	: 3	1	-1
		0.29331	0.49582	-0.21789	: 2	1	1
		0.01760	0.13211	0.01207	: 3	1	1
STATE 7:	17675.40						
		0.03449	0.18119	-0.04077	: 3	0	0
		0.06013	-0.05383	-0.23924	: 2	1	0
		0.44916	0.67020	-0.00000	: 2	1	-1
		0.44916	0.60561	-0.28705	: 2	1	1
STATE 8:	23264.19						
		0.02517	0.15867	-0.00000	: 0	0	0
		0.65290	0.80802	-0.00000	: 2	0	0
		0.01721	0.00000	0.13118	: 3	1	0
		0.12973	-0.35149	-0.07866	: 3	1	-1
		0.12973	-0.35149	0.07866	: 3	1	1
STATE 9:	25104.53						
		0.03039	0.17432	-0.00000	: 2	1	0
		0.51014	0.71424	-0.00000	: 3	1	0
		0.02897	-0.15609	-0.06789	: 2	1	-1
		0.17532	0.41676	-0.04032	: 3	1	-1
		0.02897	0.15609	-0.06789	: 2	1	1
		0.17532	-0.41676	-0.04032	: 3	1	1
STATE 10:	25315.54						
		0.04949	-0.22247	0.00000	: 2	1	0
		0.30908	0.55595	0.00000	: 3	1	0
		0.01698	-0.12969	0.01267	: 2	1	-1
		0.29458	-0.49748	-0.21700	: 3	1	-1
		0.01698	0.12969	0.01267	: 2	1	1
		0.29458	0.49748	-0.21700	: 3	1	1
STATE 11:	26347.46						
		0.06990	0.06241	-0.25691	: 4	1	0
		0.46261	0.60435	0.31205	: 4	1	-1
		0.46261	0.68015	0.00000	: 4	1	1
STATE 12:	26354.38						
		0.49878	-0.63409	-0.31099	: 4	1	-1
		0.49878	0.70624	-0.00000	: 4	1	1
STATE 13:	26354.61						
		0.92752	0.96308	0.00000	: 4	1	0

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            0.03577    0.01775   -0.18830 : 4    1   -1
            0.03577   -0.01775   -0.18830 : 4    1    1
STATE 14:  27220.87
            0.03217   -0.17937    0.00000 : 0    0    0
            0.31466    0.56094    0.00000 : 2    0    0
            0.04060    0.00000   -0.20150 : 3    1    0
            0.29848    0.53283    0.12072 : 3    1   -1
            0.29848    0.53283   -0.12072 : 3    1    1
STATE 15:  27982.88
            0.78717    0.88722   -0.00000 : 3    0    0
            0.03183    0.00000    0.17840 : 7    1    0
            0.01073   -0.00000   -0.10357 : 11    1    0
            0.01694   -0.12698   -0.02855 : 2    1   -1
            0.03079    0.07897   -0.15669 : 7    1   -1
            0.01101   -0.04228    0.09603 : 11    1   -1
            0.01694   -0.12698    0.02855 : 2    1    1
            0.03079    0.07897    0.15669 : 7    1    1
            0.01101   -0.04228   -0.09603 : 11    1    1
STATE 16:  29408.27
            0.01007   -0.07562    0.06598 : 5    1    0
            0.02799    0.12607   -0.11000 : 7    1    0
            0.46108    0.67903   -0.00000 : 5    1   -1
            0.46108   -0.09200    0.67277 : 5    1    1
STATE 17:  29414.03
            0.78621    0.88668   -0.00000 : 5    1    0
            0.08291    0.23573   -0.16535 : 5    1   -1
            0.08291   -0.23573   -0.16535 : 5    1    1
STATE 18:  29432.60
            0.16082    0.25379   -0.31051 : 5    1    0
            0.40509    0.12668    0.62373 : 5    1   -1
            0.40509    0.63646    0.00000 : 5    1    1
STATE 19:  29667.66
            0.50319    0.70936   -0.00000 : 6    1    0
            0.04930   -0.22203   -0.00000 : 7    1    0
            0.15372   -0.37015    0.12927 : 6    1   -1
            0.03142   -0.17620    0.01921 : 7    1   -1
            0.02388   -0.15375   -0.01547 : 8    1   -1
            0.15372    0.37015    0.12927 : 6    1    1
            0.03142    0.17620    0.01921 : 7    1    1
            0.02388    0.15375   -0.01547 : 8    1    1
STATE 20:  29679.13
            0.33606    0.57970    0.00000 : 6    1    0
            0.03528    0.18784    0.00000 : 7    1    0
            0.02212    0.14873    0.00000 : 8    1    0
            0.27651    0.51903   -0.08443 : 6    1   -1
            0.27651   -0.51903   -0.08443 : 6    1    1
STATE 21:  29687.15
            0.47517    0.62336   -0.29425 : 6    1   -1
            0.47517    0.68932   -0.00000 : 6    1    1
STATE 22:  29777.81
            0.13576   -0.36845    0.00000 : 6    1    0
            0.06764   -0.26007   -0.00000 : 7    1    0
            0.21523    0.46393   -0.00000 : 8    1    0
            0.04098   -0.20244    0.00000 : 9    1    0
            0.18749   -0.43073   -0.04420 : 7    1   -1
            0.04987   -0.13612   -0.17705 : 8    1   -1
            0.18749    0.43073   -0.04420 : 7    1    1
            0.04987    0.13612   -0.17705 : 8    1    1
STATE 23:  29787.25
            0.03224    0.00000    0.17957 : 3    0    0
            0.35641    0.59700    0.00000 : 7    1    0
            0.04380    0.20928   -0.00000 : 8    1    0
            0.05667   -0.23348    0.04637 : 6    1   -1
            0.03904   -0.17850   -0.08473 : 7    1   -1
            0.13676    0.36823   -0.03414 : 8    1   -1
            0.02758   -0.09033   -0.13937 : 9    1   -1
            0.05667    0.23348    0.04637 : 6    1    1
            0.03904    0.17850   -0.08473 : 7    1    1
            0.13676   -0.36823   -0.03414 : 8    1    1
            0.02758    0.09033   -0.13937 : 9    1    1
STATE 24:  29837.08
            0.29153    0.53993    0.00000 : 4    0    0
            0.02773    0.00000    0.16651 : 8    1    0
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          0.01436    0.11982    0.00244 : 6    1   -1
          0.10733   -0.31103   -0.10290 : 7    1   -1
          0.17475   -0.41278   -0.06599 : 8    1   -1
          0.02300    0.10575    0.10871 : 9    1   -1
          0.01436    0.11982   -0.00244 : 6    1    1
          0.10733   -0.31103    0.10290 : 7    1    1
          0.17475   -0.41278    0.06599 : 8    1    1
          0.02300    0.10575   -0.10871 : 9    1    1
STATE 25: 29908.82
          0.07806    0.27266    0.06096 : 4    0    0
          0.02870    0.03696   -0.16533 : 7    1    0
          0.06842   -0.05707    0.25527 : 8    1    0
          0.01822   -0.02945    0.13174 : 9    1    0
          0.30176    0.49703    0.23393 : 7    1   -1
          0.05281   -0.20767   -0.09838 : 8    1   -1
          0.03192    0.15816   -0.08311 : 9    1   -1
          0.30176    0.54933   -0.00000 : 7    1    1
          0.05281   -0.22980    0.00057 : 8    1    1
          0.03192    0.10771    0.14255 : 9    1    1
STATE 26: 30077.36
          0.02740   -0.16554    0.00000 : 7    1    0
          0.03609    0.18998    0.00000 : 8    1    0
          0.47126    0.68649    0.00000 : 9    1    0
          0.07027    0.25993   -0.05200 : 8    1   -1
          0.13469    0.36618    0.02451 : 9    1   -1
          0.07027   -0.25993   -0.05200 : 8    1    1
          0.13469   -0.36618    0.02451 : 9    1    1
STATE 27: 30089.32
          0.01309    0.11443   -0.00000 : 5    1    0
          0.09077    0.30129   -0.00000 : 8    1    0
          0.23437    0.48412    0.00000 : 9    1    0
          0.01120   -0.10582    0.00000 : 12   1    0
          0.05920    0.07013    0.23298 : 7    1   -1
          0.02921   -0.12076   -0.12092 : 8    1   -1
          0.22230   -0.45107   -0.13724 : 9    1   -1
          0.05920   -0.07013    0.23298 : 7    1    1
          0.02921    0.12076   -0.12092 : 8    1    1
          0.22230    0.45107   -0.13724 : 9    1    1
STATE 28: 30119.60
          0.01432   -0.11682   -0.02591 : 9    0    0
          0.13989    0.08100   -0.36514 : 8    1    0
          0.03727    0.18359   -0.05968 : 8    1   -1
          0.37063    0.55169    0.25742 : 9    1   -1
          0.03727    0.14113    0.13171 : 8    1    1
          0.37063    0.60879   -0.00000 : 9    1    1
STATE 29: 30238.10
          0.27033    0.51993    0.00000 : 7    1    0
          0.07159    0.26757   -0.00000 : 8    1    0
          0.02462    0.15690    0.00000 : 11   1    0
          0.03667    0.18128   -0.06168 : 7    1   -1
          0.18536   -0.39792   -0.16440 : 8    1   -1
          0.07717    0.27101    0.06103 : 9    1   -1
          0.03667   -0.18128   -0.06168 : 7    1    1
          0.18536    0.39792   -0.16440 : 8    1    1
          0.07717   -0.27101    0.06103 : 9    1    1
STATE 30: 30261.92
          0.03136    0.00000   -0.17708 : 3    0    0
          0.06029   -0.24555   -0.00000 : 7    1    0
          0.20939    0.45759   -0.00000 : 8    1    0
          0.17005   -0.41238   -0.00000 : 9    1    0
          0.01191   -0.10911   -0.00000 : 11   1    0
          0.14267    0.35812    0.12008 : 7    1   -1
          0.06098    0.19831   -0.14713 : 8    1   -1
          0.03105    0.08757   -0.15290 : 9    1   -1
          0.01753    0.12491    0.04393 : 11   1   -1
          0.14267   -0.35812    0.12008 : 7    1    1
          0.06098   -0.19831   -0.14713 : 8    1    1
          0.03105   -0.08757   -0.15290 : 9    1    1
          0.01753   -0.12491    0.04393 : 11   1    1
STATE 31: 30317.69
          0.58990    0.76805    0.00000 : 4    0    0
          0.01688    0.12993    0.00000 : 6    0    0
          0.03378   -0.00000   -0.18378 : 8    1    0
```

```
            0.13890    0.36351    0.08224 : 8    1   -1
            0.03575   -0.17291   -0.07650 : 9    1   -1
            0.13890    0.36351   -0.08224 : 8    1    1
            0.03575   -0.17291    0.07650 : 9    1    1
STATE 32: 30920.66
            0.96607    0.98289    0.00000 : 5    0    0
            0.01285   -0.11091   -0.02341 : 10   1   -1
            0.01285   -0.11091    0.02341 : 10   1    1
STATE 33: 31356.60
            0.02739    0.15916    0.04533 : 5    0    0
            0.01362    0.11224    0.03197 : 9    0    0
            0.06651    0.07065   -0.24803 : 10   1    0
            0.43435    0.56014    0.34726 : 10   1   -1
            0.43435    0.65905   -0.00000 : 10   1    1
STATE 34: 31363.61
            0.76020    0.87190    0.00000 : 10   1    0
            0.09059   -0.19295   -0.23100 : 10   1   -1
            0.01969    0.02935   -0.13722 : 11   1   -1
            0.09059    0.19295   -0.23100 : 10   1    1
            0.01969   -0.02935   -0.13722 : 11   1    1
STATE 35: 31371.99
            0.11801    0.33836   -0.05938 : 10   1    0
            0.43602    0.66032   -0.00000 : 10   1   -1
            0.43602   -0.62086    0.22485 : 10   1    1
STATE 36: 31486.86
            0.04042    0.04708   -0.19546 : 10   1    0
            0.07308    0.06330   -0.26281 : 11   1    0
            0.03706   -0.04508    0.18716 : 12   1    0
            0.39637    0.56054    0.28664 : 11   1   -1
            0.01210   -0.01249    0.10930 : 12   1   -1
            0.39637    0.62958   -0.00000 : 11   1    1
            0.01210    0.03864   -0.10300 : 12   1    1
STATE 37: 31529.21
            0.02357   -0.00000   -0.15352 : 3    0    0
            0.02682    0.00000   -0.16378 : 7    0    0
            0.03557   -0.00000   -0.18861 : 9    0    0
            0.74207    0.86143   -0.00000 : 11   1    0
            0.04816   -0.06926   -0.20824 : 11   1   -1
            0.01229   -0.02339    0.10835 : 12   1   -1
            0.04816    0.06926   -0.20824 : 11   1    1
            0.01229    0.02339    0.10835 : 12   1    1
STATE 38: 31542.32
            0.01903    0.02516    0.13562 : 3    0    0
            0.02806   -0.03056   -0.16469 : 7    0    0
            0.02312    0.02774    0.14949 : 9    0    0
            0.01601   -0.12442    0.02309 : 8    1    0
            0.02438    0.15352   -0.02848 : 11   1    0
            0.40447    0.63598    0.00000 : 11   1   -1
            0.01407   -0.00770    0.11836 : 12   1   -1
            0.40447   -0.59365    0.22814 : 11   1    1
            0.01407    0.04965    0.10772 : 12   1    1
STATE 39: 31829.64
            0.86947    0.93245    0.00000 : 6    0    0
            0.02970   -0.00000   -0.17234 : 12   1    0
            0.02634   -0.06799    0.14736 : 12   1   -1
            0.02634   -0.06799   -0.14736 : 12   1    1
STATE 40: 31984.55
            0.86362    0.92931    0.00000 : 7    0    0
            0.04157    0.00000   -0.20388 : 11   1    0
            0.01449   -0.02048   -0.11862 : 11   1   -1
            0.01632   -0.12673   -0.01621 : 12   1   -1
            0.01449   -0.02048    0.11862 : 11   1    1
            0.01632   -0.12673    0.01621 : 12   1    1
STATE 41: 32183.87
            0.03520   -0.00000   -0.18762 : 6    0    0
            0.28545    0.53427    0.00000 : 12   1    0
            0.08117    0.28491    0.00000 : 13   1    0
            0.18465   -0.40586   -0.14117 : 12   1   -1
            0.09798   -0.16475    0.26615 : 13   1   -1
            0.18465    0.40586   -0.14117 : 12   1    1
            0.09798    0.16475    0.26615 : 13   1    1
STATE 42: 32186.11
            0.01731    0.00000    0.13158 : 8    0    0
```

```
          0.39534    0.62876    0.00000 : 12    1    0
          0.02917    0.17078    0.00000 : 13    1    0
          0.02557   -0.02544    0.15788 : 11    1   -1
          0.19644    0.43564   -0.08163 : 12    1   -1
          0.02301    0.15169   -0.00141 : 13    1   -1
          0.01276   -0.02517    0.11013 : 15    1   -1
          0.02557    0.02544    0.15788 : 11    1    1
          0.19644   -0.43564   -0.08163 : 12    1    1
          0.02301   -0.15169   -0.00141 : 13    1    1
          0.01276    0.02517    0.11013 : 15    1    1
STATE 43: 32212.88
          0.04620    0.21492    0.00354 : 7     0    0
          0.01229   -0.00182    0.11084 : 11    1    0
          0.04959    0.00366   -0.22266 : 12    1    0
          0.03915   -0.00326    0.19785 : 13    1    0
          0.35426    0.59519   -0.00000 : 12    1   -1
          0.04270    0.19950    0.05387 : 13    1   -1
          0.35426    0.59487    0.01959 : 12    1    1
          0.04270    0.20117   -0.04727 : 13    1    1
STATE 44: 32222.56
          0.01584   -0.00000   -0.12585 : 8     0    0
          0.01474   -0.12140    0.00000 : 12    1    0
          0.68109    0.82528   -0.00000 : 13    1    0
          0.04650   -0.06663    0.20507 : 12    1   -1
          0.08335    0.24206   -0.15734 : 13    1   -1
          0.04650    0.06663    0.20507 : 12    1    1
          0.08335   -0.24206   -0.15734 : 13    1    1
STATE 45: 32223.36
          0.01105   -0.05856   -0.08732 : 7     0    0
          0.04140   -0.11333   -0.16900 : 8     0    0
          0.03584   -0.15723    0.10544 : 13    1    0
          0.01148   -0.09925   -0.04035 : 12    1   -1
          0.43643    0.66063    0.00000 : 13    1   -1
          0.01148    0.00034   -0.10714 : 12    1    1
          0.43643   -0.25078    0.61118 : 13    1    1
STATE 46: 32231.90
          0.90331    0.95043    0.00000 : 8     0    0
          0.01989    0.06970    0.12258 : 12    1   -1
          0.02103    0.06290   -0.13066 : 13    1   -1
          0.01989    0.06970   -0.12258 : 12    1    1
          0.02103    0.06290    0.13066 : 13    1    1
STATE 47: 32248.21
          0.05188    0.20040    0.10825 : 6     0    0
          0.11299   -0.15975    0.29575 : 12    1    0
          0.11940    0.16422   -0.30402 : 13    1    0
          0.06220    0.07523   -0.23777 : 12    1   -1
          0.28158    0.29094    0.44378 : 13    1   -1
          0.06220   -0.15760    0.19328 : 12    1    1
          0.28158    0.53064    0.00000 : 13    1    1
STATE 48: 32629.64
          0.69952    0.83638    0.00000 : 9     0    0
          0.01985   -0.00000   -0.14088 : 11    1    0
          0.05173   -0.00000   -0.22744 : 15    1    0
          0.01782   -0.05254    0.12270 : 11    1   -1
          0.03213    0.17874   -0.01350 : 14    1   -1
          0.04346   -0.07113    0.19597 : 15    1   -1
          0.01782   -0.05254   -0.12270 : 11    1    1
          0.03213    0.17874    0.01350 : 14    1    1
          0.04346   -0.07113   -0.19597 : 15    1    1
STATE 49: 33014.93
          0.32281    0.56817    0.00000 : 14    1    0
          0.30546   -0.55236   -0.01886 : 14    1   -1
          0.02242    0.00972   -0.14943 : 16    1   -1
          0.30546    0.55236   -0.01886 : 14    1    1
          0.02242   -0.00972   -0.14943 : 16    1    1
STATE 50: 33039.05
          0.64284    0.80178    0.00000 : 14    1    0
          0.17453    0.41589   -0.03951 : 14    1   -1
          0.17453   -0.41589   -0.03951 : 14    1    1
STATE 51: 33051.53
          0.05755   -0.23990   -0.00006 : 9     0    0
          0.02083    0.00004   -0.14432 : 16    1    0
          0.43956    0.66300    0.00000 : 14    1   -1
```

```
            0.01142   -0.01684    0.10555 : 16   1   -1
            0.43956    0.66300    0.00035 : 14   1    1
            0.01142   -0.01679   -0.10555 : 16   1    1
STATE 52: 33412.50
            0.50556    0.71103    0.00000 : 16   1    0
            0.19870    0.44286   -0.05078 : 16   1   -1
            0.02931    0.03490   -0.16762 : 18   1   -1
            0.19870   -0.44286   -0.05078 : 16   1    1
            0.02931   -0.03490   -0.16762 : 18   1    1
STATE 53: 33417.46
            0.02236    0.03054   -0.14639 : 14   1    0
            0.06244    0.05104   -0.24461 : 16   1    0
            0.03474    0.03807   -0.18246 : 18   1    0
            0.01619   -0.06942    0.10663 : 14   1   -1
            0.39886    0.57885    0.25256 : 16   1   -1
            0.01410    0.01135   -0.11820 : 18   1   -1
            0.01619   -0.02099   -0.12549 : 14   1    1
            0.39886    0.63155    0.00000 : 16   1    1
            0.01410   -0.03687    0.11287 : 18   1    1
STATE 54: 33481.97
            0.04512    0.00000   -0.21241 : 16   0    0
            0.32349    0.56876    0.00000 : 16   1    0
            0.02013    0.02460   -0.13974 : 14   1   -1
            0.28202   -0.48480   -0.21677 : 16   1   -1
            0.02013   -0.02460   -0.13974 : 14   1    1
            0.28202    0.48480   -0.21677 : 16   1    1
STATE 55: 33844.40
            0.01112    0.02190   -0.10316 : 3    1    0
            0.01827   -0.02807    0.13222 : 12   1    0
            0.05310    0.04785   -0.22542 : 15   1    0
            0.43470    0.60246    0.26785 : 15   1   -1
            0.43470    0.65932    0.00000 : 15   1    1
STATE 56: 33927.07
            0.48687    0.69776    0.00000 : 15   1    0
            0.01279   -0.11311   -0.00000 : 16   1    0
            0.21376    0.46153   -0.02739 : 15   1   -1
            0.21376   -0.46153   -0.02739 : 15   1    1
STATE 57: 34018.37
            0.03438    0.00000    0.18542 : 3    0    0
            0.13414   -0.00000   -0.36626 : 9    0    0
            0.33295    0.57702    0.00000 : 15   1    0
            0.23466   -0.44327   -0.19538 : 15   1   -1
            0.23466    0.44327   -0.19538 : 15   1    1
STATE 58: 34629.91
            0.80505    0.89725   -0.00000 : 10   0    0
            0.07593    0.27555    0.00000 : 11   0    0
            0.03636    0.00000   -0.19068 : 18   1    0
            0.03892   -0.07638    0.18190 : 18   1   -1
            0.03892   -0.07638   -0.18190 : 18   1    1
STATE 59: 35215.30
            0.09537   -0.30882    0.00000 : 10   0    0
            0.88084    0.93853    0.00000 : 11   0    0
STATE 60: 35446.65
            0.98095    0.99043   -0.00000 : 12   0    0
STATE 61: 35976.50
            0.93708    0.96803    0.00000 : 13   0    0
            0.03647   -0.00000   -0.19097 : 18   1    0
STATE 62: 36854.74
            0.19774    0.31486   -0.31401 : 17   1    0
            0.39599   -0.00171    0.62927 : 17   1   -1
            0.39599    0.62927    0.00000 : 17   1    1
STATE 63: 36855.85
            0.24602   -0.43651   -0.23553 : 17   1    0
            0.37143   -0.33460   -0.50939 : 17   1   -1
            0.37143    0.60945    0.00000 : 17   1    1
STATE 64: 36856.16
            0.54312    0.73697   -0.00000 : 17   1    0
            0.22249   -0.09304   -0.46242 : 17   1   -1
            0.22249    0.09304   -0.46242 : 17   1    1
STATE 65: 37383.00
            0.01093   -0.10441    0.00517 : 17   0    0
            0.01349    0.11303   -0.02674 : 18   1   -1
            0.46706    0.68342    0.00000 : 19   1   -1
```

```
            0.01349    0.11512    0.01545 : 18    1    1
            0.46706    0.68008   -0.06751 : 19    1    1
STATE 66: 37391.80
            0.16437   -0.40424   -0.03109 : 19    1    0
            0.40608   -0.62975   -0.09746 : 19    1   -1
            0.40608    0.63724    0.00000 : 19    1    1
STATE 67: 37394.31
            0.81207    0.90115   -0.00000 : 19    1    0
            0.08719   -0.29293    0.03722 : 19    1   -1
            0.08719    0.29293    0.03722 : 19    1    1
STATE 68: 37478.13
            0.01383   -0.11564   -0.02147 : 17    0    0
            0.24594    0.09052   -0.48759 : 20    1    0
            0.35187    0.55365    0.21292 : 20    1   -1
            0.35187    0.59318    0.00000 : 20    1    1
STATE 69: 37487.81
            0.10836    0.30391    0.12648 : 20    1    0
            0.43989   -0.46741   -0.47055 : 20    1   -1
            0.43989    0.66324    0.00000 : 20    1    1
STATE 70: 37489.70
            0.62554    0.79091    0.00000 : 20    1    0
            0.18565    0.32802   -0.27937 : 20    1   -1
            0.18565   -0.32802   -0.27937 : 20    1    1
STATE 71: 37667.09
            0.70750    0.84113   -0.00000 : 14    0    0
            0.20293    0.45048   -0.00000 : 15    0    0
            0.02206   -0.14853    0.00000 : 16    0    0
            0.01915    0.00000    0.13838 : 18    1    0
            0.01775    0.00855    0.13296 : 18    1   -1
            0.01775    0.00855   -0.13296 : 18    1    1
STATE 72: 37691.25
            0.26381   -0.51362   -0.00000 : 14    0    0
            0.67745    0.82307    0.00000 : 15    0    0
            0.01923    0.00000    0.13868 : 18    1    0
            0.01399   -0.00392    0.11823 : 18    1   -1
            0.01399   -0.00392   -0.11823 : 18    1    1
STATE 73: 37722.48
            0.08016    0.00000   -0.28313 : 10    0    0
            0.02135    0.00000   -0.14611 : 11    0    0
            0.13926   -0.00000    0.37318 : 17    0    0
            0.25641    0.50637    0.00000 : 18    1    0
            0.01290    0.11357    0.00000 : 20    1    0
            0.20512   -0.42399   -0.15922 : 18    1   -1
            0.01018   -0.01725    0.09939 : 20    1   -1
            0.20512    0.42399   -0.15922 : 18    1    1
            0.01018    0.01725    0.09939 : 20    1    1
STATE 74: 37786.90
            0.03479   -0.03588   -0.18304 : 16    1    0
            0.04786   -0.04209   -0.21468 : 18    1    0
            0.01329   -0.03231   -0.11066 : 16    1   -1
            0.41090    0.64101    0.00000 : 18    1   -1
            0.01174   -0.08771    0.06361 : 19    1   -1
            0.01329    0.01187    0.11467 : 16    1    1
            0.41090    0.59357   -0.24202 : 18    1    1
            0.01174   -0.10523   -0.02579 : 19    1    1
STATE 75: 38011.79
            0.02397    0.00000   -0.15484 : 1     0    0
            0.04696    0.00000   -0.21670 : 13    0    0
            0.10810   -0.00000    0.32878 : 15    0    0
            0.42452    0.65156    0.00000 : 18    1    0
            0.02323    0.03157   -0.14910 : 16    1   -1
            0.15784    0.39576   -0.03484 : 18    1   -1
            0.02323   -0.03157   -0.14910 : 16    1    1
            0.15784   -0.39576   -0.03484 : 18    1    1
STATE 76: 38515.37
            0.01556    0.12473    0.00000 : 14    0    0
            0.90464    0.95113   -0.00000 : 16    0    0
            0.01233   -0.00000   -0.11103 : 1     1    0
            0.01740    0.00000   -0.13192 : 16    1    0
            0.01474   -0.04961    0.11083 : 16    1   -1
            0.01474   -0.04961   -0.11083 : 16    1    1
STATE 77: 38734.78
            0.83156    0.91190    0.00000 : 17    0    0
```

```
          0.05279    0.00000    0.22975 : 18    1    0
          0.04406    0.08670   -0.19116 : 18    1   -1
          0.04406    0.08670    0.19116 : 18    1    1
STATE 78: 40069.20
          0.99809    0.99905    0.00000 : 18    0    0
STATE 79: 40834.70
          0.99967    0.99984    0.00000 : 19    0    0
STATE 80: 42709.88
          0.99604    0.99802   -0.00000 : 20    0    0
```

Table S16. TD-DFT excited states (triplets) of **LBi**. Note that the correction factor of 1430 cm^{-1} has not been subtracted from these values.

```
STATE  1: E=  0.058568 au      1.594 eV    12854.3 cm**-1 <S**2> =   2.000000
  139a -> 140a :     0.994482

STATE  2: E=  0.075348 au      2.050 eV    16536.9 cm**-1 <S**2> =   2.000000
  139a -> 141a :     0.979703

STATE  3: E=  0.105853 au      2.880 eV    23232.2 cm**-1 <S**2> =   2.000000
  139a -> 142a :     0.607670
  139a -> 147a :     0.343252
  139a -> 151a :     0.023850

STATE  4: E=  0.112851 au      3.071 eV    24767.8 cm**-1 <S**2> =   2.000000
  130a -> 148a :     0.016915
  133a -> 140a :     0.789563
  133a -> 152a :     0.010244
  134a -> 141a :     0.108363
  139a -> 148a :     0.013040

STATE  5: E=  0.126881 au      3.453 eV    27847.2 cm**-1 <S**2> =   2.000000
  131a -> 140a :     0.027160
  134a -> 140a :     0.056754
  137a -> 141a :     0.022053
  138a -> 140a :     0.795634

STATE  6: E=  0.128159 au      3.487 eV    28127.7 cm**-1 <S**2> =   2.000000
  133a -> 141a :     0.047510
  134a -> 140a :     0.756336
  138a -> 140a :     0.064908
  139a -> 143a :     0.018597
  139a -> 152a :     0.014694

STATE  7: E=  0.128649 au      3.501 eV    28235.1 cm**-1 <S**2> =   2.000000
  139a -> 143a :     0.858966
  139a -> 149a :     0.039603
  139a -> 150a :     0.026113

STATE  8: E=  0.129833 au      3.533 eV    28495.1 cm**-1 <S**2> =   2.000000
  131a -> 142a :     0.015993
  134a -> 140a :     0.032970
  135a -> 144a :     0.061591
  135a -> 145a :     0.148998
  135a -> 146a :     0.022829
  136a -> 144a :     0.105859
  137a -> 142a :     0.032881
  137a -> 143a :     0.126891
  137a -> 145a :     0.010384
  137a -> 146a :     0.054866
  138a -> 142a :     0.211385
  138a -> 143a :     0.022167
  138a -> 147a :     0.038989
  139a -> 145a :     0.010220

STATE  9: E=  0.130079 au      3.540 eV    28549.1 cm**-1 <S**2> =   2.000000
  131a -> 143a :     0.011675
  135a -> 144a :     0.110194
  136a -> 144a :     0.057236
  136a -> 145a :     0.143242
  136a -> 146a :     0.027550
  137a -> 142a :     0.176335
  137a -> 143a :     0.017524
  137a -> 147a :     0.036811
  138a -> 140a :     0.035016
  138a -> 142a :     0.027580
  138a -> 143a :     0.149267
  138a -> 145a :     0.011772
  138a -> 146a :     0.062135
  139a -> 143a :     0.013938
  139a -> 144a :     0.018725
```

STATE 10: E= 0.135658 au 3.691 eV 29773.4 cm**-1 <S**2> = 2.000000
133a -> 140a : 0.018603
139a -> 144a : 0.660668
139a -> 147a : 0.013087
139a -> 148a : 0.260566

STATE 11: E= 0.135942 au 3.699 eV 29835.7 cm**-1 <S**2> = 2.000000
139a -> 145a : 0.135110
139a -> 146a : 0.686982
139a -> 149a : 0.107177
139a -> 150a : 0.035619

STATE 12: E= 0.139034 au 3.783 eV 30514.5 cm**-1 <S**2> = 2.000000
139a -> 142a : 0.357763
139a -> 144a : 0.022434
139a -> 147a : 0.593320

STATE 13: E= 0.139587 au 3.798 eV 30635.7 cm**-1 <S**2> = 2.000000
139a -> 145a : 0.816607
139a -> 146a : 0.156263

STATE 14: E= 0.143261 au 3.898 eV 31442.1 cm**-1 <S**2> = 2.000000
133a -> 140a : 0.018949
134a -> 141a : 0.011990
139a -> 144a : 0.279035
139a -> 148a : 0.653932

STATE 15: E= 0.145923 au 3.971 eV 32026.5 cm**-1 <S**2> = 2.000000
139a -> 143a : 0.057657
139a -> 145a : 0.017725
139a -> 146a : 0.102935
139a -> 149a : 0.737854
139a -> 154a : 0.017116

STATE 16: E= 0.146040 au 3.974 eV 32052.0 cm**-1 <S**2> = 2.000000
129a -> 140a : 0.012342
131a -> 141a : 0.014245
137a -> 140a : 0.562302
138a -> 141a : 0.334822
138a -> 148a : 0.018512
139a -> 149a : 0.012785

STATE 17: E= 0.160656 au 4.372 eV 35259.8 cm**-1 <S**2> = 2.000000
128a -> 140a : 0.012827
133a -> 140a : 0.100076
134a -> 141a : 0.737031
134a -> 148a : 0.026194
139a -> 148a : 0.040995

STATE 18: E= 0.161321 au 4.390 eV 35405.9 cm**-1 <S**2> = 2.000000
132a -> 140a : 0.955460

STATE 19: E= 0.163114 au 4.439 eV 35799.4 cm**-1 <S**2> = 2.000000
135a -> 140a : 0.195577
136a -> 140a : 0.494458
136a -> 141a : 0.020546
136a -> 142a : 0.017693
136a -> 143a : 0.013904
136a -> 144a : 0.023104
136a -> 146a : 0.016620
137a -> 144a : 0.019790
137a -> 145a : 0.023183
138a -> 142a : 0.018524
138a -> 144a : 0.031782
138a -> 145a : 0.030744

STATE 20: E= 0.163558 au 4.451 eV 35896.8 cm**-1 <S**2> = 2.000000
135a -> 140a : 0.559091
135a -> 141a : 0.019758
135a -> 144a : 0.032867
135a -> 145a : 0.027715
136a -> 140a : 0.229059
136a -> 144a : 0.012130

137a -> 142a : 0.015230
138a -> 142a : 0.023709
138a -> 143a : 0.013543

Table S17. Calculated SOC values between singlet and triplet states.

T	S	SOCC [cm^{-1}]	T	S	SOCC [cm^{-1}]	T	S	SOCC [cm^{-1}]	T	S	SOCC [cm^{-1}]	T	S	SOCC [cm^{-1}]
1	0	26.83311	5	0	397.6778	9	0	97.80565	13	0	96.35074	17	0	41.3826
1	1	2.19399	5	1	177.64771	9	1	55.46283	13	1	13.70316	17	1	324.41473
1	2	10.41983	5	2	292.03547	9	2	100.56979	13	2	34.0816	17	2	51.5662
1	3	21.8098	5	3	43.53696	9	3	261.59614	13	3	16.72996	17	3	15.64712
1	4	7.15322	5	4	48.70459	9	4	77.03597	13	4	48.50421	17	4	117.86572
1	5	371.79368	5	5	12.92731	9	5	14.66328	13	5	14.82044	17	5	16.48043
1	6	33.41163	5	6	53.38891	9	6	88.70327	13	6	49.68993	17	6	47.60928
1	7	4.86608	5	7	59.48738	9	7	15.05226	13	7	7.75728	17	7	5.23506
1	8	0.15906	5	8	11.16436	9	8	2.26641	13	8	3.88497	17	8	2.29691
1	9	8.69295	5	9	70.32624	9	9	281.32981	13	9	6.37957	17	9	21.25126
1	10	911.36856	5	10	72.30723	9	10	21.9953	13	10	11.83115	17	10	85.23678
1	11	404.36085	5	11	73.10031	9	11	40.48139	13	11	26.88064	17	11	90.95756
1	12	7.17468	5	12	162.34168	9	12	53.76313	13	12	3.73229	17	12	10.57685
1	13	125.87966	5	13	34.7857	9	13	16.9662	13	13	3.20729	17	13	49.37412
1	14	492.56199	5	14	22.47869	9	14	6.42767	13	14	9.33639	17	14	5.36703
1	15	290.46776	5	15	17.75834	9	15	4.85012	13	15	6.16838	17	15	10.39066
1	16	3327.38822	5	16	139.56278	9	16	42.72356	13	16	49.55118	17	16	28.31362
1	17	424.52991	5	17	82.44264	9	17	84.01717	13	17	44.44679	17	17	28.93222
1	18	36.93732	5	18	49.2605	9	18	22.86508	13	18	13.47784	17	18	4.70894
1	19	23.48185	5	19	14.6851	9	19	15.87441	13	19	6.56415	17	19	33.80238
1	20	20.27605	5	20	62.03222	9	20	54.86588	13	20	6.77242	17	20	46.13395
2	0	15.95271	6	0	154.90373	10	0	126.71493	14	0	189.00125	18	0	203.88134
2	1	11.95276	6	1	80.23935	10	1	18.96171	14	1	24.29609	18	1	3391.14153
2	2	30.32504	6	2	120.17273	10	2	44.07545	14	2	116.19608	18	2	166.02289
2	3	1907.02482	6	3	92.02018	10	3	76.90144	14	3	186.9744	18	3	7.22835
2	4	184.15462	6	4	33.00677	10	4	11.48394	14	4	23.42354	18	4	8.84472
2	5	156.90476	6	5	44.68251	10	5	77.22131	14	5	66.58275	18	5	18.88284
2	6	287.52447	6	6	43.87365	10	6	43.14532	14	6	14.52553	18	6	26.96372
2	7	12.27026	6	7	22.22157	10	7	7.51745	14	7	20.48778	18	7	66.58902
2	8	8.35756	6	8	3.71046	10	8	3.54105	14	8	4.26597	18	8	18.57816
2	9	820.43826	6	9	51.77319	10	9	128.0144	14	9	112.35861	18	9	6.59143
2	10	201.19065	6	10	186.66035	10	10	20.82729	14	10	13.33264	18	10	799.59221
2	11	668.15469	6	11	70.95001	10	11	115.50359	14	11	36.10969	18	11	364.42196
2	12	86.55348	6	12	49.53984	10	12	16.18695	14	12	19.78203	18	12	67.99519
2	13	32.65644	6	13	21.01646	10	13	5.53069	14	13	7.60076	18	13	483.96278
2	14	16.53231	6	14	64.97819	10	14	0.70915	14	14	8.84707	18	14	32.11692
2	15	9.37148	6	15	35.96149	10	15	0.99217	14	15	5.05512	18	15	100.96981
2	16	110.10416	6	16	438.01647	10	16	33.16623	14	16	32.18198	18	16	18.63376
2	17	560.13031	6	17	53.9982	10	17	50.23569	14	17	31.88468	18	17	346.33043
2	18	5.27061	6	18	22.51801	10	18	14.20347	14	18	24.58591	18	18	28.33688
2	19	49.50693	6	19	13.24714	10	19	32.50799	14	19	28.25059	18	19	4.84897
2	20	359.30363	6	20	30.46173	10	20	14.57756	14	20	33.40717	18	20	45.78987
3	0	5777.57286	7	0	877.63189	11	0	1051.11011	15	0	1353.08836	19	0	13.13959
3	1	115.76494	7	1	29.45266	11	1	57.52831	15	1	18.13825	19	1	236.3925
3	2	1721.13956	7	2	665.28881	11	2	650.64183	15	2	1077.15088	19	2	1.27177
3	3	26.66755	7	3	657.98441	11	3	760.62217	15	3	1035.25864	19	3	63.19293
3	4	430.71268	7	4	41.43113	11	4	7.03246	15	4	14.64489	19	4	59.38279
3	5	4.39958	7	5	11.65951	11	5	14.93244	15	5	11.353	19	5	4.79402
3	6	472.45722	7	6	48.74294	11	6	9.0621	15	6	15.34602	19	6	82.41373
3	7	250.26885	7	7	113.45051	11	7	122.75815	15	7	174.45929	19	7	122.04842
3	8	23.89626	7	8	4.23491	11	8	3.63264	15	8	4.32864	19	8	136.81434
3	9	11.3281	7	9	313.95846	11	9	348.10779	15	9	471.25024	19	9	73.52391
3	10	392.58974	7	10	28.72867	11	10	4.81083	15	10	5.90523	19	10	56.82089
3	11	869.54461	7	11	35.98258	11	11	18.13636	15	11	25.75797	19	11	51.07657
3	12	157.62232	7	12	125.81572	11	12	101.42708	15	12	146.08496	19	12	25.57452
3	13	18.04241	7	13	31.32318	11	13	33.676	15	13	31.98176	19	13	37.90094
3	14	3.37837	7	14	2.32284	11	14	8.89264	15	14	13.02396	19	14	13.47265
3	15	1.29634	7	15	5.88147	11	15	4.77638	15	15	6.99429	19	15	10.64664
3	16	1.68932	7	16	54.45303	11	16	48.07489	15	16	65.73325	19	16	26.1605
3	17	30.77876	7	17	39.34291	11	17	6.33199	15	17	10.0018	19	17	80.80391
3	18	273.12562	7	18	107.46141	11	18	88.66528	15	18	64.60244	19	18	2.3951
3	19	180.60865	7	19	8.11338	11	19	5.61699	15	19	4.20625	19	19	10.8517
3	20	172.05948	7	20	120.92238	11	20	116.76808	15	20	160.49878	19	20	10.60217
4	0	21.96191	8	0	68.1547	12	0	1244.96378	16	0	274.51593	20	0	13.01172

4	1	15.0447	8	1	21.89023	12	1	162.05842	16	1	1133.57488	20	1	49.6832
4	2	15.07499	8	2	51.32505	12	2	422.43808	16	2	21.38328	20	2	12.45687
4	3	91.60129	8	3	112.44791	12	3	33.07049	16	3	144.0737	20	3	84.34729
4	4	26.26889	8	4	220.74793	12	4	115.77395	16	4	12.95481	20	4	71.19747
4	5	27.35872	8	5	13.58239	12	5	1.0741	16	5	117.3274	20	5	3.91102
4	6	10.85921	8	6	257.7854	12	6	115.66964	16	6	16.50722	20	6	85.74628
4	7	1.79279	8	7	9.5143	12	7	57.05422	16	7	25.64437	20	7	36.88208
4	8	0.86597	8	8	6.06623	12	8	10.88109	16	8	72.97134	20	8	13.22583
4	9	44.2144	8	9	109.00067	12	9	14.60036	16	9	67.20633	20	9	90.92689
4	10	1.47041	8	10	18.61066	12	10	70.86397	16	10	15.70271	20	10	23.53338
4	11	19.91127	8	11	114.49093	12	11	223.48397	16	11	15.24855	20	11	47.09154
4	12	8.67657	8	12	21.98593	12	12	35.26729	16	12	104.67036	20	12	11.17464
4	13	2.77188	8	13	13.34829	12	13	32.87002	16	13	21.14478	20	13	13.83872
4	14	2.88739	8	14	12.087	12	14	7.26702	16	14	135.1859	20	14	2.01303
4	15	1.55425	8	15	7.52513	12	15	3.73296	16	15	84.39028	20	15	2.6353
4	16	21.78224	8	16	83.18027	12	16	5.59387	16	16	912.59757	20	16	12.57625
4	17	4.24727	8	17	197.79934	12	17	6.6235	16	17	10.78593	20	17	90.31819
4	18	0.80703	8	18	9.1597	12	18	179.05802	16	18	59.07472	20	18	2.39167
4	19	7.49961	8	19	39.99299	12	19	40.46077	16	19	0.40853	20	19	12.72116
4	20	29.6821	8	20	6.2454	12	20	94.76074	16	20	481.94567	20	20	11.1208

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